ADSORPTION OF DYES BY CLAY MINERALS AND ITS APPLICATION TO COLOUR REMOVAL

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
V. V. SETHU RAMAN

to the
DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST 1973

CERTIFICATE

This is to certify that the present work titled, " ADSORPTION OF DYES BY CLAY MINERALS AND ITS APPLICATION TO COLOUR REMOVAL " has been carried out by Sri V.V. SETHURAMAN under my supervision and the work has not been submitted elsewhere for a degree.

DR. B.C. RAYMAHASHAY
Assistant Professor

POST GRADUATE OFFICE
This thesis has been approved
for the award of the Degree of
Master of Technology (M.Tech.)
in accordance with the
regulations of the Indian
Institute of Technology Kanpur
Dated. 20.8.73

POST GRADUATE OFFICE
Submitted on 13/8/73

ACKNOWLEDGEMENT

I wish to express my sincere gratitude to Dr. B.C. Raymahashay for his able and inspiring guidance for carrying out this study. I render my heartfelt thanks to all the Faculty members of the Sanitary & Environment family for their valuable advices from time to time.

I also acknowledge with thanks :

1. C.S.I.R. (Grant No. 7/92/(247)/71-GAU-I) for the financial aid during the period of study.

2. Authorities of Elgin Mills, Kanpur and in particular Mr. T.N.Sharma, Managing Director for providing the dye sample and their cooperation in obtaining the dye waste.

3. Dr. Madhav Rao, Geology Lab., for his help in carrying out X-ray and D.T.A studies.

4. All my colleagues in the Sanitary and Environmental Engineering Laboratory for all the assistance rendered by them.

V.V. SETHURAMAN

I.I.T. KANPUR
CENTRAL LIBRARY
Acc. No. A 26205

V
JUNE '76

24 SEP 1973

Thesis
667.14
Se75

CE-1973-M-RAM-ADS

CONTENTS

		PAGE
LIST OF TABLES		i.
LIST OF FIGURES		ii.
ABSTRACT		
CHAPTER: I	INTRODUCTION	
	1.1 Necessity for Colour Removal	1
	1.2 Colour Causing Components of Industrial Waters	4
	1.3 Recommended Colour Limits	5
	1.4 Methods for Colour Removal	7
	1.5 Background of Present Study	11
CHAPTER: II	LITERATURE REVIEW & OBJECTIVE	
	2.1 Review of Textile Dye Waste Treatment	13
	2.2 Adsorption on Clays	15
	2.2.1 Structure of Clay Minerals	15
	2.2.2 Origin of Surface Charge in Clays	17
	2.2.3 Ion Exchange	19
	2.2.4 Surface Area	21
	2.2.5 Adsorption of Dyestuffs by Clays	21
	2.2.6 Adsorption of Other Organic Compounds by Clays	23
	2.3 Objective	24

CHAPTER : III EXPERIMENTAL STUDY

3.1 Materials 25

3.2 Apparatus 27

3.3 Preparation of Pure Clays 28

3.4 Experimental Procedure 29

CHAPTER : IV RESULTS & DISCUSSION

4.1 Kinetics of Adsorption 32

4.1.1 Methylene Blue Adsorption on Kaolinite 32

4.1.2 Methylene Blue Adsorption on Montmorillonite 32

4.1.3 Sulfur Blue Adsorption on Clay Minerals 33

4.1.4 Adsorption of Dyes on Activated Carbon 40

4.2 Adsorption - Desorption Studies 40

4.2.1 Methylene Blue - Clay Systems 40

4.2.1.1 X-ray Observations 47

4.2.1.2 D.T.A. Data 48

4.2.2 Sulfur Blue - Clay Systems 52

4.2.3 Effect of P^H on Adsorption 53

4.2.4 Adsorption on Activated Carbon 53

4.3 Comparison of Adsorption Capacities of Clay Minerals & Activated Carbon 57

4.4 Coagulation of Sulfur Blue Dye by Lime 58

4.5 Colour Removal of Sulfur Dye Waste 58

4.6 Significance of Adsorption-Desorption Data in Stream Pollution Studies 60

4.7 Suggestions for Future Study 61

CHAPTER :	V	CONCULSIONS	62
CHAPTER :	VI	BIBLIOGRAPHY	64
APPENDIX:	A	Data for Freundlich Isotherm for Physical Adsorption in Excess of C.E.C. of Clays	
APPENDIX:	B	Data for Freundlich Isotherm for Dyes-Activated Carbon Systems.	

LIST OF TABLES

			PAGE
TABLE :	1	Toxicity of Various Chemicals Used in Textile Industry	3
TABLE :	2 (a)	Colour Limits For Domestic Water Supply	5
TABLE :	2 (b)	Colour Range For Raw Water Sources of Domestic Water Supply	5
TABLE :	3	Colour Limits for Industrial Waters	6
TABLE :	4	% Colour Removal of Dye Waste by Various Processes	10
TABLE :	5 (a)	Adsorption - Desorption Studies of Methylene Blue - Montmorillonite System	42
	(b)	Methylene Blue Kaolinite System	42
TABLE :	6	Analysis of Sulfur Blue Dye Waste	59
TABLE :	7	% Colour Removal of Sulfur Dye Waste by Various Materials	59

LIST OF FIGURES

FIG: 1 Atom Arrangement in Unit Cell of Kaolinite

FIG: 2 Atom Arrangement in Unit Cell of Montmorillonite

FIG: 3 Standard Curves for Dyes

FIG: 4 Kinetics of Methylene Blue Adsorption on Karolinite

FIG: 5 Kinetics of Methylene Blue Adsorption on Montmorillonite

FIG: 6 Three Stages of Methylene Blue Adsorption on Montmorillonite

FIG: 7 Kinetics of Sulfur Blue Adsorption on Kaolinite

FIG: 8 Kinetics of Sulfur Blue Adsorption on Montmorillonite

FIG: 9 Kinetics of Adsorption of Dyes on Activated Carbon

FIG: 10 Kinetics of Adsorption Of Dyes on Activated Carbon on $(\text{Time})^{\frac{1}{2}}$ Scale.

FIG:11 Adsorption-Desorption of Methylene Blue-Montmorillonite System

FIG:12 Adsorption - Desorption of Methylene Blue - Kaolinite System

FIG:13 Freundlich Isotherm for Physical Adsorption of Methylene Blue - Clays Systems

FIG:14 X-Ray Observations of Methylene Blue Kaolinite System

FIG:15 X-Ray Observations of Methylene Blue-Montmorillonite System

FIG:16 D.T.A of Methylene Blue - Montmorillonite System

FIG:17 Effect of P^H on Adsorption of Methyle Blue - Clays Systems

FIG:18 Freundlich Isotherm for Adsorption of Dyes on Activated Carbon

ABSTRACT

This thesis presents data on the adsorption of two dyes, Methylene Blue (cationic) and Sulfur Blue (anionic) by three different adsorbents, viz., Kaolinite Clay, Montmorillonite clay and Activated Carbon. The experiments were designed to study two aspects: (1) Kinetics and (2) Parameters. These led to some conclusions about the mechanism of the adsorption processes.

Methylene Blue is adsorbed at continuously decreasing rates from 10 mg/g.min to 0.07 mg/g.min by monbuorillonite, 16 mg/g.min by kaolinite and 0.36 mg/g.min by activated carbon. The adsorption capacities for this dye are 0.72 m.eq/g in the case of montmorillonite, 0.32 m.eq/g for kaolinite and 0.21 m.eq/g for activated carbon.

The adsorption of Methylene Blue is irreversible (no desorption) up to a level of 60 m.eq/100 g of montmorillonite and 5 m.eq/100 g of kaolinite. These numbers are exactly equal to the cation Exchange Capacity (CEC) of the clay minerals. For dye concentrations above these levels, the adsorbed dye can be readily desorbed in distilled water until the adsorbed concentration falls back to CEC. These data support the existing hypothesis that clay minerals remove Methylene Blue from aqueous solutions by an irreversible Chemisorption (Ion Exchange) up to the CEC level and by reversible Physical Adsorption beyond this level.

The higher adsorption by montmorillonite is obviously due to its higher CEC which in turn is related to inter layer adsorption. This mechanism was indicated by X-ray studies and confirmed by Differential Thermal Analysis. Sulfur Blue is adsorbed at the rate of 2.3 mg/g. min Kaolinite, 2.6 mg/g. min by montmorillonite and 0.3 mg/g. min by Activated carbon. The rate and amount of Sulfur Blue adsorption are less than that of Methylene blue for all the three adsorbents. The adsorptive capacities of Kaolinite, montmorillonite and activated carbon for this dye are 0.053 m.eq/g , 0.066 m.eq/g and 0.063 m.eq/g respectively. The adsorption of Sulfur Blue on clay minerals was apparently through Anion Exchange and was found to be irreversible.

Colour removal from dye waste of the Elgin Mills, Kanpur was 42% by Maolinite, 50% by montmorillonite and 48% by activated carbon. A preliminary comparation study of Lime Coagulation indicated 94% removal.

CHAPTER : I

INTRODUCTION:

Surface waters may become coloured by the discharge of certain Industrial wastes, notable among them being wastes from Dyeing operations in Textile Industry. Colour is the most common yardstick by which a common man judges pollution of streams.

1.1 NECESSITY FOR COLOUR REMOVAL

Following are some of the factors necessiating the removal of colour causing compounds present in water bodies.

(1.1.1) DEVELOPMENT OF COMMUNITY

Colour which causes visible pollution retards the development of a community. It discourages the recreational fecilities like camping, boating, swimming, fishing etc. which are indispensable to the vitality of a physically and mentally healthy community. Property values decrease along a visibly polluted river.

(1.1.2) AESTHETIC IMPORTANCE:

Consumers will complain if the public water supply is coloured as it is aesthetically unacceptable.They will shun such a supply and may prefer waters from uncontrolled springs or private wells eventhough, these may not be safe from hygienic point of view. Industries discharging coloured wastes into rivers will lose public relation and reputation

(1.1.3) EFFECT ON RECEIVING STREAMS

(1.13.1) TOXICITY:

The combination of chemicals used in various processes in Textile Industries often produce a toxic condition in receiving streams. These are not only destructive to fish and aquatic life but also have the effect of killing the bacteria and various other forms of biological life upon which the stream self purification processes depend (Ref. Table: 1)

(1.1.3.2) INCREASE IN B.O.D. LOADING AND DEPLETION OF DISSOLVED OXYGEN:

Textile dye wastes have a B.O.D loading ranging from 0.5 to 32 Kg/1000 Kg cloth. When discharged into rivers, the organic constituents decompose resulting in the removal of dissolved oxygen needed for the support of the aquatic bacterial life. Continuous depletion of dissolved oxygen creates septi conditions leading to putrefication, accompanied by unsightly odour and colour.

(1.1.3.3) EFFECT ON PHOTOSYNTHESIS:

Colour interferes with the transmission of light into the stream and therefore lessens photosynthetic activity. It may also interfere with oxygen absorption from the atmosphere although no positive proof of this action exists.

(1.1.3.4) HEATED DISCHARGE OF INDUSTRIAL WASTES:

Dye wastes are discharged at elevated temperature. Warm waters have a decreased capacity for dissolving oxygen and hence aquatic life is affected.

TABLE : 1.

TOXICITY OF VARIOUS CHEMICALS USED IN TEXTILE INDUSTRY (R.K. SOUTHERS)[1].

CHEMICALS	CONCENTRATION As	p.p.m.	TEST ORGANISM	EFFECT
Chromic acid	Cr	0.3	Dalphnia nagma	Toxic
Hydrochloric acid	HCl	63	- do -	- do -
Nitric acid	HNO_3	107	- do -	- do -
Sulfuric acid	H_2SO_4	88	- do -	- do -
Cadmium chloride	Cd	0.01	Gold-fish	Kills in 9-18
Cadmium sulphate	Cd	513	Minnows	Kills in 3 hrs.
Copper sulphate	Cu	0.8	Gold-fish	Kills in 24-96
- do -	Cu	0.04	Dalphnia magma	Toxic
Sodium chromate	Cn	0.1	- do -	- do -
Sodium Sulphide	S	5	Gold-fish	Toxic
Sulphide (ion)	S	3	Trout	Kills in 5 mins.
Chromate (ion)	Cr	20	Gold-fish	Kills in 8 days
- do -	Cr	0.01	Microflora	Toxic
Ferric chloride	Fe	34	Gold-fish	Kills in 1-1.5
Ferric sulphate	Fe	336	Gold-fish	Kills in 2-10
Zinc sulphate	Zn	25	Trout	Kills in 4-5
Zinc (ion)	Zn	0.1	Fish	Kills fresh fish in 2 hrs.
Potassium cyanide	CN	0.04-0.12	Goldfish	Kills in 3-4
Cyanogen chloride	CNCl	0.08	Fish	Critical
Stannous chloride	Sn	626	Gold-fish	Kills in 4-5

(1.2) COLOUR CAUSING COMPONENTS OF INDUSTRIAL WATERS:

For most of the industries, colour as harmful, when the water is to be used in processing units. Colour causes staining problem in textiles. Manganese, as low as 0.2 mg/l may cause dark brown or black spots on the fabrics. Iron is detrimental in production of wastes for Brewing Industry, as it gives bad flavour and causes disscolouration of beer. Coloured wastes produces tinges and " off colours" in pulp and paper mills. In tanneries, it affects the quality of the leather. Food products are contaminated by the organics in water. In Dye-houses, laundries and Rayon plants, it is practically impossible to operate, with an iron bearing water because of colour problem. In boiler feed water conditioning, the organics render the analysis of water, very difficult by masking end points and colour comparisons. Organic pollutants may also provide an environment favourable to the growth of slime and algae in water mains, recirculating system etc. These may cause clogging action and cut down the flow rates. Thus colour in industrial wastes has a bearing on the economics of the industries.

(1.3) RECOMMENDED COLOUR LIMITS

(1.3.1) COLOUR LIMITS FOR DOMESTIC WATER SUPPLY:

TABLE : 2 (a)

COMPONENT	U.S. PUBLIC HEALTH SERVICE DRINKING WATER STANDARDS (1962)	COMMITTEE ON PUBLIC HEAL ENGG. MINISTRY OF HEALTH GOVT. OF INDIA (1962)	
	PERMISSIBLE * COLOUR UNITS	PERMISSIVE HAZEN UNITS	EXCESSIVE **
Colour	20	5	25
Iron as Fe mg/l	0.3	0.3	1.0
Manganese as Mn mg/l	0.05	0.1	0.5

TABLE: 2 (b)

COLOUR RANGE FOR RAW WATER SOURCES OF DOMESTIC WATER SUPPLY[2]

SOURSE	RANGE OF COLOUR UNITS*
Excellent sourse of water supply, requiring dissinfection only as treatment	0-20
Good sourse of water, requiring conventional treatment	20-150
Poor sourse of water supply, requiring conventional and special treatment and disinfection	$>$ 150

* 1 colour unit = colour produced by 1 mg/l platinum as K_2PtCl_6

** 1 Hazen unit (Pt-CoSCale) = colour produced by a mixture of 1 mg/l Pt (or 2.49 mg/l K_2PtCl_6) and 2 mg/l of $CoCl_2.6H_2O$.

(1.3.2) COLOUR LIMITS FOR INDUSTRIAL WATERS:

Table 3 gives the tolerance limits for colour and its components in water of various industrial use.

TABLE : 3

WATER FOR	U.S. Public Health service 1962				I.S. code of practice				
	Colour	Fe:	Mn:	Fe & Mn together	Colour	Fe:	Mn:	Fe & Mn	Specification
	Colour Units	mg/l	mg/l	mg/l	Hazen Unit	mg/l	mg/l	mg/l	
Baking	10	-	-	-	-	-	-	-	-
Boiler Feed water	2-80	(according to various pressure)							
Bottled Bevarages	5-10								
Brewing	0-10				10	-	-	-	IS 4700-1968
Food processing	5-10	0.2	0.2	0.3	20	0.3	0.2	-	IS 4251-1964
Food products	10	0.2	0.2	0.2	20	0.2	0.2	-	Do
Food equipment washing	5-20	0.2	0.2	0.2	20	0.2	0.2	-	Do
Ice Manufacturing	0-5	0.3	0.2	0.2	5	0.3	0.2	0.2	IS 3957-1964
Nitro-cellulose products	1	0.1	0.05	0.1	-	-	-	-	-
Pulp & Paper	0-10	0.1	0.05	0.1	20	0.2	0.1	0.2	IS 2724-1964
Tanning plastics	10-50	0.1	2.0	0.1-0.2, 0.2	25	-	-	1.0	IS 4221-1967
Textiles	0-25	0.25	0.1	0.25	20	0.25	0.1	0.25	IS 201-1964

(1.3.3) Chrisco[51] et al have suggested that a colour of 100 units in cobalt-platinum scale is satisfactory for industrial wastes to be discharged into the receiving water bodies.

(1.4) METHODS FOR COLOUR REMOVAL:

(1.4.1) PHYSICAL METHODS:

(1.4.1.1) EQUALIZATION:

Coloured industrial wastes vary in composition and concentration. Textile dye waste often contain both acidic and alkaline materials. The holdin period and mixing in an equalization tank permit partial self neutralization, thus decreasing the requirements of chemical reagent for further treatment. Equalization of temperature is also accomplished by this process.

(1.4.1.2) DILUTION:

The intensity of coloured wastes can be reduced by dilution with water to an acceptable limit and can be directly discharged into the streams without any other form of treatment. If the volume of the wastes is small and the pollutional load is less, then natural dilution takes place in the river course.

(1.4.1.3) SEDIMENTATION:

This process removes only the settleable particles and hence a portion of " Apparent colour". It does not remove dissolved or colloidal colour. Sedimentation helps in removing a part of suspended matter and reduces the quantity of chemicals to be used in later processes. In pulp and paper mills, sedimentation removes short fibres and fillers present in "white water", thus recovering useful materials and also preventing stream pollution.

(1.4.1.4) FILTRATION:

Filtration removes a part of Apparent colour by transferring suspended solids onto grains of sand, coal or any other filtering material. Slow and rapid sand filtrations are used in water treatment field to remove colour by about 30 %. Filtration also removes iron and manganese, the later precipitates slowly and responds better to slow than to rapid filtration.

(1.4.2) CHEMICAL METHODS:

(1.4.2.1) COAGULATION:

Coagulation removes colloidal colour. True colour exists in primarily as negatively charged particles. They can be removed by coagulation with the aid of iron salts, alum, calcium chloride and lime. Colour colloids coagulate best in the acidic range. Coagulant aids are used to speed up coagulation and to reduce the coagulant dosages.

(1.4.2.2) CHEMICAL PRECIPITATION:

Certain coloured metallic ions can only be removed by chemical precipitation, fcllowed by sedimentation or filtration. Iron and manganese can be precipitated by the addition of lime or soda ash.

(1.4.2.3) OXIDATION:

Oxidation of organic pollutants leads to the formation of harmless end products. Common oxidising agents are chlorine, bleaching powder, ozone, sodium nitrate, potassium permangnate and dichromate and hydrogen peroxide.

(1.4.3) BIOLOGICAL METHODS:

One of the most effective methods of treating organic contaminants is by the action of bacteria and other microorganisms.

(1.4.3.1) AEROBIC BIOLOGICAL TREATMENT:

This includes trickling filters (low and high rate,multi stage) Activated sludge (Tapered aeration, step aeration, dispersed growth aeration) Bisorption, oxidation ditches etc.

(1.4.3.2) ANAEROBIC BIOLOGICAL TREATMENT:

This includes anaerobic digester, sceptic tank, anaerobic lagoons, etc.

(1.4.3.3) AEROBIC AND ANAEROBIC BIOLOGICAL TREATMENT:

Fécultative oxidation ponds and lagoons belong to this category. Table :4 shows the % colour removal of dye wastes by different methods.

(1.4.4) ADSORPTION:

Adsorption is the process by which dissolved substances are removed from the solution and concentrated on the surface of certain materials, called Adsorbents. In water and waste-water treatment, activated carbon, bauxite Fuller's earthand various clay minerals, magnesia, silica gel and activated silica are employed as adsorents.

TABLE : 4

% colour removal of dye wastes by various processes (R.K.Southers[3])

I COAGULATION

Dye waste	Chemical	% colour reduction
Direct dyes	Alum	75
	$FeCl_3$	85.0
	$FeSO_4$ + Lime	90.0
Indigo	Lime	65.0
	$FeSO_4$ + Lime	94.5
	Alum	65.0
	$CaCl_2$	94.5
Napthol	H_2SO_4	99
	Alum	99.5
	$FeCl_3$	99.5
Sulfur	H_2SO_4	99.0
	Alum	99.0
	$FeSO_4$	99.7

BIOLOGICAL METHODS:

WASTE	METHOD	% COLOUR REDUCTION
25% Sulfur and Indigo dye waste + 75% sewage	Trickling filters	40
75% dye waste + 25% sewage	-do-	38.6
50% dye waste + 50% sewage	Activated sludge	83.3
40% dye waste + 60% sewage	Lagoon	62-63

(1.5) BACKGROUNFD OF PRESENT STUDY:

(1.5.1) CHOICE OF INDUSTRY:

Some of the industries discharging coloured wastes are Textiles, Leather, Pulp and Paper mills, Tanneries etc. Among these textile industry was chosen for this study as it is one of the largest industries in Kanpur. Among the various wastes from textiles, dye wastes draw the attention of the Public Health officials and also the public opinion, as it is highly coloured. Removal of colour from dye wastes is important from stream pollution abatement point of view.

(1.5.2) CHOICE OF METHOD:

Among the various methods listed in section (1.4) Adsorption has been preferred for the study. Physical processes remove only a fraction of colour. Chemical methods involve cost of chemicals, fecilities for chemical feeding and personnel for operation and maintenance and hence an expensive process. Biological processes are handicapped by the presence of toxic materials in dye wastes which inhibit the growth of the microbial population. Moreover, Biological methods do not remove the colour completely and further treatment like clorination is necessary. Adsorption on clay minerals is a cheap method and overcomes the draw backs of other methods.

(1.5.3)

CHOICE OF ADSORBENT:

Among the various commercial adsorbents, clay minerals were chosen because of the low cost of treatment involved. Clay minerals have a large surface area per unit weight of the order of 100 m^2/g. In natural water system, clay minerals play the role of an adsorbent for dissolved chemicals in water. Rivers and streams ahving a high content of suspended solids of which clay minerals comprise a significant amount, may transport chemicals, biological wastes and gases adsorption at the clay water interface. Suspended or dissolved constituents in natural or wastewater infiltrating the soil, may react with the clay minerals by adsorption. Clays thus perform the role of a decontamination device in both the natural waters and soil horizons. Clay minerals are very inexpensive as compared with other adsorbents like activated carbon. Also clays do not require any pretreatment before its application. Hence clay minerals were chosen as the adsorbents for the present study.

CHAPTER: II

LITERATURE REVIEW AND OBJECTIVE

(2.1) Review of Textile Dye waste Treatment.

Various methods of treating dye-wastes for colour removal have been listed in Chapter: I. Among these, physical methods involve much less expenditure. McCarthy[4] showed that a judicious mixture of various vat dye wastes precipitated a considerable amount of B.O.D. by equilization giving an un-offensive colour and p_H of the effluent. Nemerov[5] suggested neutralization of dye-wastes before discharge into municipal sewers.

Chemical coagulation is the most effective method for the removal of colour from dye-wastes, but is an expensive method and should be avoided wherever possible. Till 1920, the most commonly used coagulants were alum, lime, copperas and sulfuric acid. Alum and acid coagulation were found to be unsatisfactory because of foaming and H_2S evolution respectively. $CaCl_2$ overcame these problems and was used from thereon, either alone or in combination with other coagulants. Porges[6] found that rapid mixing with little flocculation effected better colour removal and also suggested that Acid treatment of sludge might recover the dyes and the coagulants. Smallhorst[7] observed that aeration of the waste before chemical coagulation gave better results.

Biological oxidation of dye-wastes separately and in combination with domestic sewage has been found feasible. For smal volume of waste, Activated sludge process (dispersed growth or endogenous respiration) is efficient. For larger volume of waste with varying strength, Trickling filter works very well, due to its ability of absorbing shock loads.

The efficiency of trickling filter is reduced by 10 to 40 % at high pH values of the waste. Southers[8] found that a mixture of upto 40 % of dye waste with domestic sewage can be successfully treated, with no chemical pH adjustment, by a combination of high rate Trickling filter and Activated sludge units, but high percent values of dye-wastes, the sewage organisms were inhibited by the constituents of dye-wastes. Geyer[9] suggested that batch process will be economical than continuous treatment, when the waste volume was less than 0.3 MGD. Lagoons have been found to remove colour and B.O.D. appreciably and also convert hydroxide alaklinity into carbonate and bi - carbonate alkalinity reducing the pollutional load. Clarification of the wastes after chemical and biological treatments, by sedimentation is necessary to prevent sludge accumulation on the bottom and banks of the receiving stream.

Beach[10] used CO_2 from the flue gases to precipitate sulfur dye-wastes. Various adsorbents have been used to remove colour compounds from dye-wastes. Thronton and Moore[11] used Fuller's earth and Activated Bauxite. They found that certain dyes adsorbed more easily than others. Regeneration of adsorbent and recovery of certain dyes have been found possible. Adsorption on Activated carbon was found successful by Snell[12] and Mudri[13] but its high cost is a disadvantage. Rak[14] used cinder and flyash to adsorb dye-wastes. In another study, he subjected the dye-wastes to the action of direct current which caused the organics to be oxidised at the anode leaving the effluent practically colourless.

Ragan[15] used Evaporation as a method for treatment of dye-wastes. He found that if the evaporation rate per year is 20" or more than the average rainfall per year, then this method would be useful.

Michelson[16] employed Foam fractionation using a cationic surfactant to remove the colour from dye wastes. The chemical cost was estimated at $ 210 to treat 1 MGD of waste. Todd and Hopper[17] recovered 93-97 % Azo dyes by solvent extraction. Williamson[18] handled dye wastes in a municipal plant and found that chlorination after alum coagulation removed a high % of colour. He also achieved excellent results with chlorination ahead of Trickling filter units. In a recent study Aurich[19] adopted ultra-filtration through dynamically formed membranes and reported high removal of colour from Nylon dye-wastes.

(2.2) ADSORPTION ON CLAYS:

(2.2.1) STRUCTURE OF CLAY MINERALS:

Clay minerals are primarily hydrated silicates of aluminium or magnesium on which unit layers are arranged in stacks. There are two broad classes:

1) Two layers silicates (e.g., Keolinite)
2) Three Layer silicates (e.g., Montmorillonite)

This classification is based on the linking of two fundamental structural units:

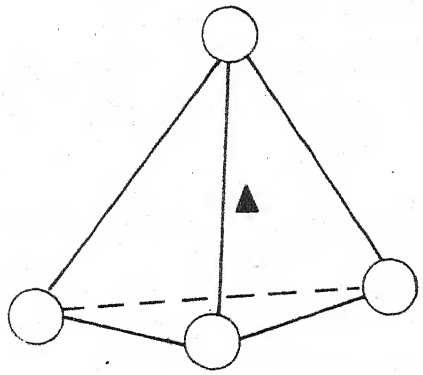
1) The silica sheet or the tetrahedral layer in which each silicon atom is surrounded by four oxygen atoms in a tetrahedral coordination.

2) The Gibbsite (or Brucite) sheet or the octahedral layer in which six oxygen or hydroxyl atoms surround one Aluminium (or Magnesium) atom in an octahedral coordination.

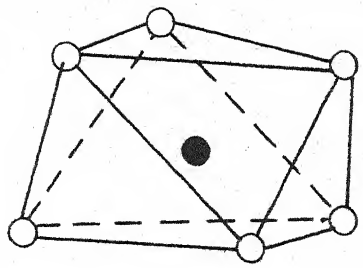
The oxygen atoms in both the tetrahedral and octahedral layers are linked in a hexagonal array. The dimensions are such that these layers can be superimposed in two or three layers packets with the oxygen atoms at the tips of the tetrahedra jointly shared by the octahedral layer.

In the Kaolinite structure, a single tetrahedral layer and a single octahedral layer are combined with a common layer of tetrahedral and octahedral atoms (Grim[20] 1953), ref. Fig: 1.) The unshared oxygens in the octahedral layers are OH groups. The units are continuous in the a and b crystallographic directions and stacked one above the other in the 'c' (vertical) direction. The unit layer (2 layer tetrahedral-octahedral group) is 5 atoms thick and the repeat distance in the c direction (basal spacing) is 7.38 A°.

The montmorillonite structure is composed of units made up of two silica tetrahedral sheets with central alumina octa-hedral sheet sandwitched between the silica sheets. The combination is such that the tips of the tetrahedron of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layers become O instead of OH (ref. Fig. 2) The layers are continuous in the a and b directions and are stacked one above the other in the c direction.



Silica tetrahedron



Alumina octahedron

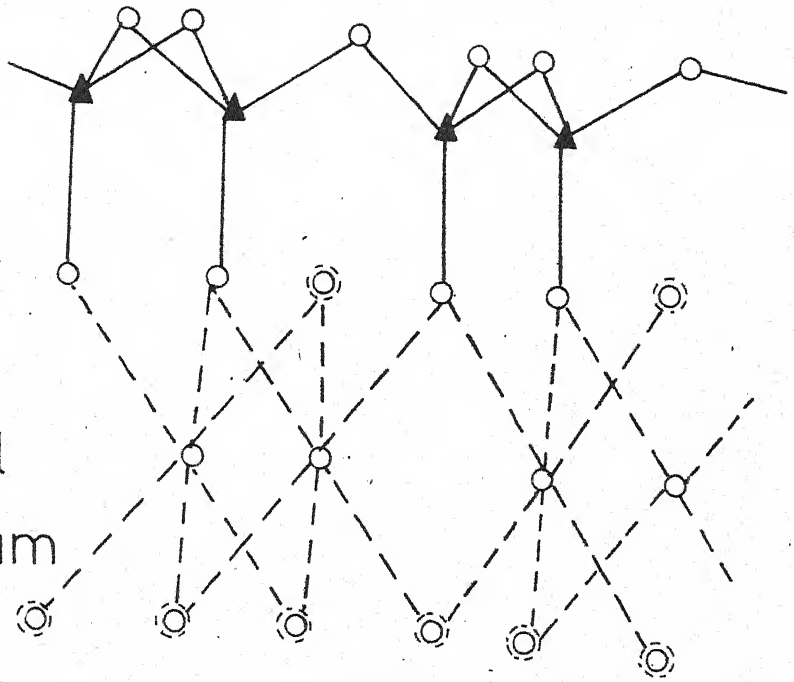


FIG. 1 ATOM ARRANGEMENT IN UNIT CELL OF KAOLONITE

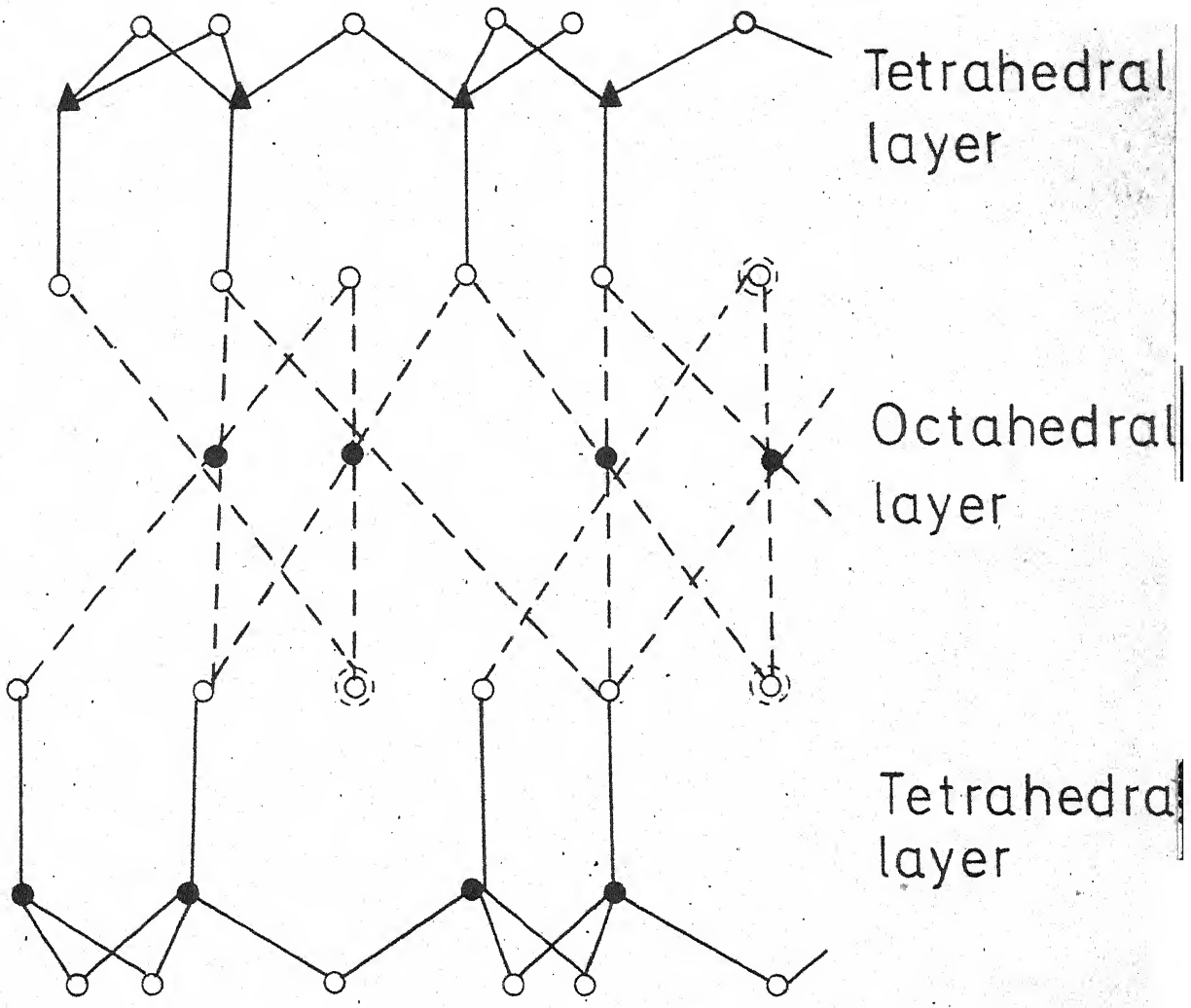


FIG. 2 ATOM ARRANGEMENT IN UNIT CELL OF MONTMORILLONITE

In the stacking of silica-alumina-silica units, o layers of each unit are adjacent to o layers of the neighbouring units, with the consequence that, there is a weak bond and an excellent cleavage between them. The outstanding feature of the montmorillonite structure is that water and other polar molecules can enter between the unit layers, causing the lattice to expand. The minimum repeat distance in the c direction for montmorillonite is 9.6 A°, when no polar molecules are present in the interlayer, but because of the presence of exchengeable cations and water in the interlayer, the c spacing is usually of the order of 14A°. The basal spacing is variable due to interlayer swelling.

(2.2.2) ORIGIN OF SURFACE CHARGE IN CLAYS:

There are three mechanisms believed to be responsible for charge phenomenon on clay mineral surfaces. They are given below :

(2.2.2.1) ISOMORPHOUS SUBSTITUTION:

Substitutions within the lattice structure of trivalent Aluminium for quadrivalent silicon, in the tetrahedral sheet and of ions of lower valency, like Mg for Al, in the octahedral layer., result in unbalanced charges in the structural unit of clay minerals. Sometimes such substitutions are balanced by other lattice changes, e.g., OH for O or by filling more than two thirds of the possible octahedral positions.

(2.2.2.2) BROKENBONDS:

Brokenbonds along crystalline edges of clay particles, parallel to the C axis would also give rise to unsatisfied charges. Bonds may be broken either in the tetrahedral or octahedral layer.

In the octahedral layer, the situation would involve Al - O - Al - O. If the severance is between Al and O, then a site is created with a positive charge. If bonds are broken between O and Al, then the site becomes negative, as a result of the exposed oxygen (generally of an OH ion). The same type of reasoning can be applied to the tetrahedron layer edges wherein the bonding is Si - O - Si - O.

(2.2.2.3) LATTICE DEFECTS:

The recent hypothesis for origin of charge especially for Kaolinite, is a mechanism creating negative charges from lattice defects.[21] It is believed that an interlayer between the Si and Al layers is possible, because of similarity in thicknesses of these layers. It is indicated that, if holes in the lattice were attributed to a deficit of 0.15 %, then a negative charge could arise. An alternative approach suggests that Al might be in a tetrahedral coordination with oxygen rather than in octahedral coordination.

(2.2.3) ION EXCHANGE:

Clay minerals have the property of adsorbing certain cations and Anions and retaining them in an exchangeable state. The exchangeable ions are held around the outside of the silica alumina clay mineral units, and the exchange reaction generally does not affect the structure of the silica alumina packet.

(2.2.3.1) CATION EXCHANGE:

In the case of kaolinite, the cations exchange is mostly due to "broken bonds", around the edges of the silica-alumina units. These unsatisfied changes are balanced by external cations present on the edges of the kaolinite, to preserve electrical neutrality. The number of broken bonds and hence the exchange capacity would increase as the particle size is decreased. Lattice distortions would tend to increase broken bonds and hence the cation exchange would be increasing as the degree of crystallinity is decreased. Isomorphous substitution in the structural unit of kaolinite also has contribution towards cation exchange.

For montmorillonite, 80 % cation exchange capacity is due to isomorphous substitution in the lattice structure and 20 % due to broken bonds. The unbalanced charges are satisfied by exchangeable cations present mostly on the basal cleavage surface of the clay mineral and also on the edges.

The cation exchange capacity (C.E.C) of kaolinite varies from 3 - 15 meq/100 g and for montmorillonite from 80 - 150 meq/100g[22].

(2.2.3.2) ANION EXCHANGE:

Vanolphen[23] has proposed a dual charge on clay, in terms of the electrical double theory. He suggested that a negative double layer exists along the faces and a positive double layer occurs on the edge of the particle,not-withstanding the overall effect of a net negative charge on the clay minerals. Clay minerals are amphotric in nature possessing both cation and Anion sites for exchange, confirmed by the presence of both positive and negative broken bonds at the crystal edges. At low pH values, some OH ions ionise away from the surface leaving a positively charge site. Thes OH ions, under some circumstances may be replaced by other ions. At neutral or high pH values,the OH groups remain firmly attached to the surface and only the cations ionize away from the surface to expose negative sites. The overall net negative charge explains the higher cationic exchange capacity on faces in comparison to the observed low values of anionic exchange occuring most likely on the edges.

The investigation of anion exchange reaction is very difficult, because of the possibility of decomposition of clays during the course of the reaction. In the studies of Adsorption of Phosphates by Kaolinite, there is disagreement in the conslusions,as to whether the observed results are due to adsorption,or due to the replacement of OH ions in the kaolinite

lattice by phosphate ions or to a precipitation or complexing of phosphate with clay mineral.

It has been found that Anion exchange in montmorillonite does not take place on the basal plane surfaces.

(2.2.4) SURFACE AREA:

Since adsorption is a surface phenomenon, the extent of adsorption is proportional to the specific surface area. The surface area can be increased by decreasing the size of the clay particles and also by acid treatment. The observed specific surface area for kaolinite ranges from 10 - 25 m^2/g and for montomorillonite it is about 40 - 100 m^2/g.[24].

(2.2.5) ADSORPTION OF DYESTUFFS BY CLAYS:

Dyestuffs are strongly ionizing organic compounds. A basic dye like Methylene blue ionizes in aqeous medium to form a dye cation and a simple anion as shown below:

$$C_{16}H_{18}N_3S.Cl \rightleftharpoons C_{16}H_{18}N_3S^+ + Cl^-$$

The dye cation thus formed is readily exchanged for the cations present in the clays.

Pleach and Robertson[25] found this " ion exchange adsorption" taking place till the C.E.C. of the clay was reached. When the dye was added in excess of the C.E.C, Physical adsorption was taking place till an equlibrium was reached between the adsorbed and the unadsorbed dye.

Faruqi[26] et al showed that the ion exchange adsorption was irreversible by carrying adsorption - desorption studies. Fairbairn[27] observed that for kaolinite and montmorillonite, the physically adsorbed dye in excess of C.E.C of the clays was 13 % and 10 % of the C.E.C of the clays respectively The amount of dye irreversibly held by the clay has been used as a measure of surface area, cation exchange capacity and minerological composition of the clays by many investigators (Robertson and Ward[28], Ramachandran,[29] Nevins[30], Kipling[31] and Worall[32]) in the fields of medicine, ceramics, metallurgy and soil mechanics. In a study on the relative exchange strength on pretreated clays, Markert[33] found that for kaolinite and bentonite the order is $MB^+ > H^+ > K^+ > Ca^{++}$ and for Illite, $Ca^{++} > MB^+ > H^+ > K^+$.

Anionic dyes ionize in solution forming a complex dye anion and an inorganic cation.

e.g. C.I. Sulphur Blue 11, $C_{12}H_6(NO_2)_2NSOH \rightleftharpoons C_{12}H_6(NO_2)_2NSO^- + H^+$

The dye anion is adsorbed on the positive sites at the edges of the clay minerals. Only a small proportion of the acidic dye has been found to be irreversibly adsorbed because of the low values of the anion exchange capacity of clays. Allingham and Cullen[34] found that the adsorption of anionic dyes on Lochaline sand was less and slow. Fialkov[35] found that acidic dyes were adsorbed more on acid treated clays than untreated clays.

Acid and alkali treatment of various clays have been carried out by many workers to improve the dye adsorption capacity of clays. (Tsuchiya[36], Mocik[37], Kwun[38], Merabishvilli[39] and Hofman)[40]

Thermal analysis was used by Ramachandran et al[41] and Leontleva[42] to employ the adsorption of dyes on clays as a basis for identifying clay minerals. Kaolinite-Methylene blue and Montmorillonite-dye complex show a characteristic exothermal peaks at 350 - 435°C and 650 - 700°C respectively.

In a recent study, Ivanova[43] observed two types of adsorption of dyes on clays.

1) Electrovalent bonding between the dye cation and the clay surface, replacing the inorganic ion.

2) H-bond formation of dyes on active hydroxyl group minerals.

(2.2.6) ADSORPTION OF OTHER ORGANIC COMPOUNDS BY CLAYS:

The uptake of organic compounds like surfactants, glucose, alcohols, amines, ammonium compounds, antibiotics, pesticides etc. by clays also showed the ion exchange adsorption behaviour as outlined in section (2.2.5). The adsorption of polar organic molecules on montmorillonite is characterised by the inter-layer swelling and increase in basal spacing. This has been confirmed by X-ray observations by many workers (Giesiking[44], Greenland[45], Allaway and Grim[46], McEwan[47] and Hellen and Bodenheimer[48]). Organic clad clay minerals are changed from hydrophyllic to hydrophobic nature and find various application in different fields

like gelling agents in lubricants, fillers and strengthening agents in plastic, as components of printing ink , as flattening agents in paints and for soil stabilization for roads and run-ways and conditioning for agricultural use.

(2.3) OBJECTIVE:

From a review of dye adsorption on clays it was observed that in most of the studies, the clay used was not in the natural condition but in a particular form like Na^+ clay, H^+ clay, Ca^+ clay etc. In order to resemble the natural condition of the sediments of the streams and the soils, the clay minerals have been used in the original form without any acid or alkali treatment. The inherent nature of the clay surface and the changes imposed on it by dyestuffs must be assessd in order to evaluate the adsorption characteristics of clays.

In short the objectives of the present study can be stated as follows:

1) To study the Kinetics of Adsorption of dyes on clay minerals.

2) To determine the parameters of adsorption and to explore the possibility of using clay minerals for colour removal.

3) To investigate the mechanism of dye adsorption on clay minerals.

4) To compare the performance of clay minerals with that of Activated carbon.

CHAPTER : III

EXPERIMENTAL STUDY:

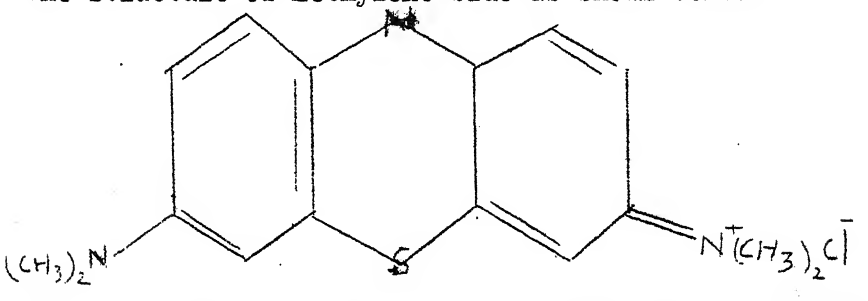
(3.1) MATERIALS:

(3.1.1) DYESTUFFS:

(3.1.1.1) METHYLENE BLUE: (BDH grade)

(MOLECULAR WEIGHT = 319.87)

The structure of methylene blue is shown below:



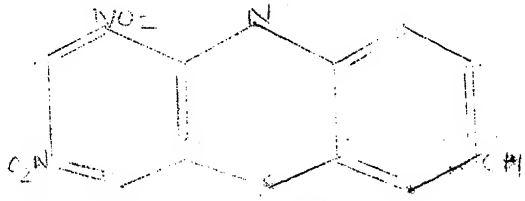
This dye belongs to the basic dyestuff group. It has thiazine group as chromophore, with methyl groups in positions 3 and 9 auxochromes. It is soluble in water and alcohol. It was used as colorants for paper. Tannin-mordanted cotton and silk. It is a very important biological stain and as a free base, finds internal use as a medicine.

(3.1.1.2) THIONOL DIRECT BLUE RL 450

C-I Sulphur blue 11, 53235. (Molecular Weight = 305)

This dye belongs to the sulphur dyestuffs classification. It was obtained from Elgin Mills, Kanpur, where it is used widely for dyeing cotton. This dye is manufactured by Imperial Chemical Industries (India) Pvt. Ltd.,

It is prepared by the aqueous sulfurization of p,2,4, (dinitroaniline) phenol and has the following structure.



It has thiazine as the chromophore and OH group as Auxochrome. It is used in the water soluble form by alkaline reduction with sodium sulfide.

(3.1.2) CLAY MINERALS

Kaolinite and Montmorillonite were used as adsorbents in the present study. They were obtained from Industrial minerals and chemicals company, Bombay.

X-ray observations showed the presence of small amounts (approximately 20% total) of illite, montmorillonite and Quartz in the kaolinite sample and traces of kaolinite in the montmorillonite. The average size of the clay minerals was found with the help of Fisher subsieve sizer. These values are 1.6 μ and 2.4 μ for kaolinite and montmorillonite respectively.

The C.E.C. of clay minerals was determined by saturating the clays with H^+ ions and titrating with NaOH. (Black[53]). The values were found to be 5 and 60 m.eq/100 g for kaolinite and montmorillonite respectively.

(3.1.3) Laxmi activated carbon, Najibabad, U.P.

Grade: LC/16-32, Ref. 3310

(3.1.4) Lime, CaO (Laboratory chemical)

(3.2) APPARATUS:

The following apparatus were used in carrying out the experiments:

(3.2.1) Bauch and Lomb Spectronic - 20, calorimeter/spectrophotometer
Bauch and Lomb company Rochester, Newyork, U.S.A.

(3.2.2) Beckman Expandometic pH meter
Beckman Industrial Company, California, U.S.A.

(3.2.3) Elico pH meter, Model L1 - 10
Electronic and Industrial Instrument Co. Pvt. Ltd., Hyderabad, India

(3.2.4) Sorvall, SS-3, Automatic Superspeed Centrifuge
Irvan Sorwall Inc. U.S.A.

(3.2.5) Fisher Sub-sieve Sizer
Fisher Scientific and Company, U.S.A.

(3.2.6) XR-DC X-ray Diffractometer
General Electric Company, Wisconsin, U.S.A.

(3.2.7) Jar Test Apparatus
Phillips and Birol, Inc. Richard

(3.2.8) Du Pont 900 Differential Thermal Analyser
Wilmington, U.S.A.

(3.2.9) Laboratory Shaker .

(3.3.) PREPARATION OF PURE CLAYS:

Bulusu[49] in his study on colour removal of pulp and paper waste by adsorption on Black cotton soil reported poor settleability and the problem of separating clay from the supernatant solution. He found that filtration through whatman No. 42 filter paper did not remove the clay particles, which caused turbidity in the supernantant, hampering the analytical procedure for colour estimation.

To overcome this problem the clay minerals were suspended in distilled water and allowed to settle in a vertical glass jar for about 12 hrs. After gravitational settling the top most portion of the clay suspension, containing the finely divided clay particles was removed. The remaining supernatant containing only clay particles was pipetted out and dried at 105°C for one hour to get the pure form of clays. The bottom most portion containing the coarser particles like Quartz and silt was discarded. Thus the finer portion of clays which cause turbidity and the coarser impurities were elliminated. The medium sized clay suspension could be removed from the clay dye complex easily by centrifuging

(3.4) ANALYTICAL METHOD FOR DETERMINING THE CONCENTRATION OF DYE:

Colometric method was employed for estimating the dye concentration during adsorption experiments. The apparatus used was Bauch and Lomb Spectronic-20.

The optimum wavelengths for methylene blue and Sulfur Blue were found to be 620 mμ and 580 mμ respectively.

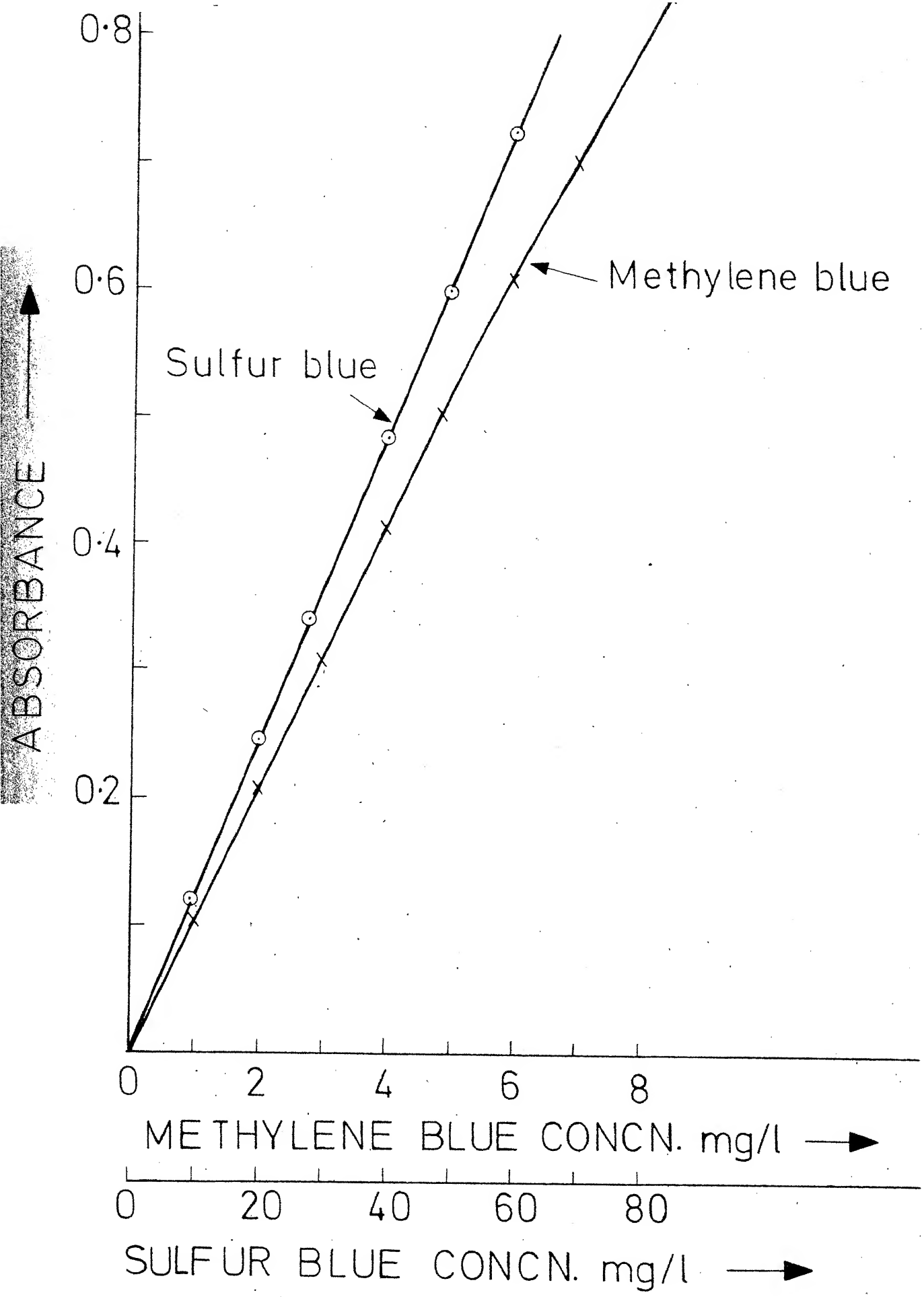


FIG. 3 STANDARD CURVES FOR DYES

Standard calibration curves for the dyes were prepared by plotting the absorbance values at optimum wavelength against a range of concentrations of the dye solutions. Fig : 3 shows the standard curve for methylene blue and sulphur blue dyes.

(3.5) EXPERIMENTAL PROCEDURE:

Batch technique was used to evaluate the rate and equilibrium of adsorption of dyes on clay minerals.

(3.5.1) RATE OF ADSORPTION:

The rate study was conducted in a series of 1 litre wide mouth pyrex bottles. Predetermined amounts of pure kaolinite and montmorillonite were added to one litre volume of aqueous dye solutions of 100 mg/l concentration of both dyes. The test solutions were agitated in a laboratory shaker. The temperature was maintained at 23 ± 1°C. At frequent time intervals, an aliquot of dye solution was withdrawn and diluted if necessary. It was centrifuged at 5000 rpm for 10 minutes to separate the clay present in the aliquot. The dye remaining in solution was determined colorimetrically. From this, the amount of adsorbed dye can be found out.

The amount of dye adsorbed was plotted with respect to time.

(3.5.2) ADSORPTION EQUILIBRIA:

The equilibrium study was conducted in several 300 ml. volume pyrex bottles. In each bottle, 200 ml of both dye solution of 100 mg/l concentration was taken. Accurately weighed quantities of both clay minerals were added to each series of bottles. The amount of clay added was varied to cover the range of desired equlibrium solute concentrations. The test solutions were agitated in a laboratory shaker till the system equlibriated.

(3.5.3) EFFECT OF pH:

The effect of pH of dye solution on adsorption was studied by gradually increasing the pH of the dye solution by 1 N NaOH to desirable ranges and the experiment was conducted as in (3.5.2)

(3.5.4) DESORPTION:

After the equlibrium of adsorption was attained, the clear supernatant in the reaction flask was decanted and the remaining portion was centrifuged to separate the dye adsorbed clay from the aqueous system. This clay was then re-suspended in 200 ml of distilled water. The test solution was then agitated in a laboratory shaker. The dye coming out of the clay was determined by the increase in the concentration of dye in distilled water, at different time intervals till the dye concentration in distilled water did not increase any more.

(3.5.5) ADSORPTION ON ACTIVATED CARBON:

The adsorption of dyes on activated carbon was carried out in the same way as for clays.

(3.5.6) COAGULATION BY L I M E:

Jar test apparatus was used for coagulation study of lime. 500 ml of 100 mg/l concentration of both the dye solutions were taken in six 1 litre beakers separately. The dose of lime was varied from 50 mg/l to 300 mg/l in stages. The optimum dose of lime was found out by the standard procedure (Sawyer)[50]

CHAPTER: IV

RESULTS AND DISCUSSION.

(4.1) KINETICS OF ADSORPTION:

(4.1.1) METHYLENE BLUE ADSORPTION ON KAOLINITE

The rate of adsorption of Methylene blue on Kaolinite appears to be very fast. Within 5 minutes of contact with 1.0 g/l of Kaolinite, the concentration of dye decreased from 100 mg/l to 20 mg/l. The concentration of dye remaining in solution did not decrease any further after one hour shaking with Kaolinite (Fig. 4). The rate of adsorption is 16 mg/g. min. The rate study suggests that large fraction of the clay's absorptive capacity is being saturated within a very short period of time.

(4.1.2) METHYLENE ADSORPTION ON MONTMORILLONITE

The rate of adsorption of Methylene blue on montmorillonite is slower than that of Kaolinite. On shaking with 1 g/l montmorillonite, the dye remaining in solution is reduced from an initial concentration of 100 mg/l to 50 mg/l in 5 minutes. After one hour contact, the dye concentration in solution is 20 mg/l and at the end of 2 hours, when equilibrium is attained, it is 16 mg/l (Fig: 5). The rate of adsorption decreased from 10 mg/g. min. in the first 5 min to 0.55 mg/g.min in the next hour and finally 0.07 mg/g.min.

When the amount of dye adsorbed is plotted against square root of time as shown in (Fig: 6) three distinct stages of rate of Methyle blue adsorption on montmorillonite can be observed,

The first stage is accompanied by instantaneous adsorption when the dye cations are exchanged for the inorganic cations of the clay and deposited on the surface of the clay particle. The second stage is achieved by gradual adsorption when the montmorillonite is slowly expanded by the diffusion of dye cation into the intercellular spaces of the clay mineral indicating interlayer adsorption. The third stage shows the equilibrium adsorption.

(4.1.3) SULFUE BLUE ADSORPTION ON CLAY MINERALS:

The rate of sulfur blue adsorption on both clay minerals is slower than that of Methylene blue. The rate of adsorption of sulfur blue on Kaolinite is 2-3 mg/g-min (Fig: 7) as compared with 16 mg/g-min for Methylene blue - Kaolinite system. The rate of adsorption of sulfur blue on montmorillonite is 2.6 mg/g-min. (Fig: 8) and did not vary as was the case in Methylene blue montmorrilonite system. The rate study suggests that the sylfur blue on both clay minerals is limited only to the surface of the clay minerals. As the adsorption of sulfur blue on clay minerals is due to anion exchange, and as the anions in clays are only on the surface and edges of the clays, no inter-layer adsorption of sulfur blue was found to occur on montmorrillonite, unlike that of the methylene blue-montmorillonite system.

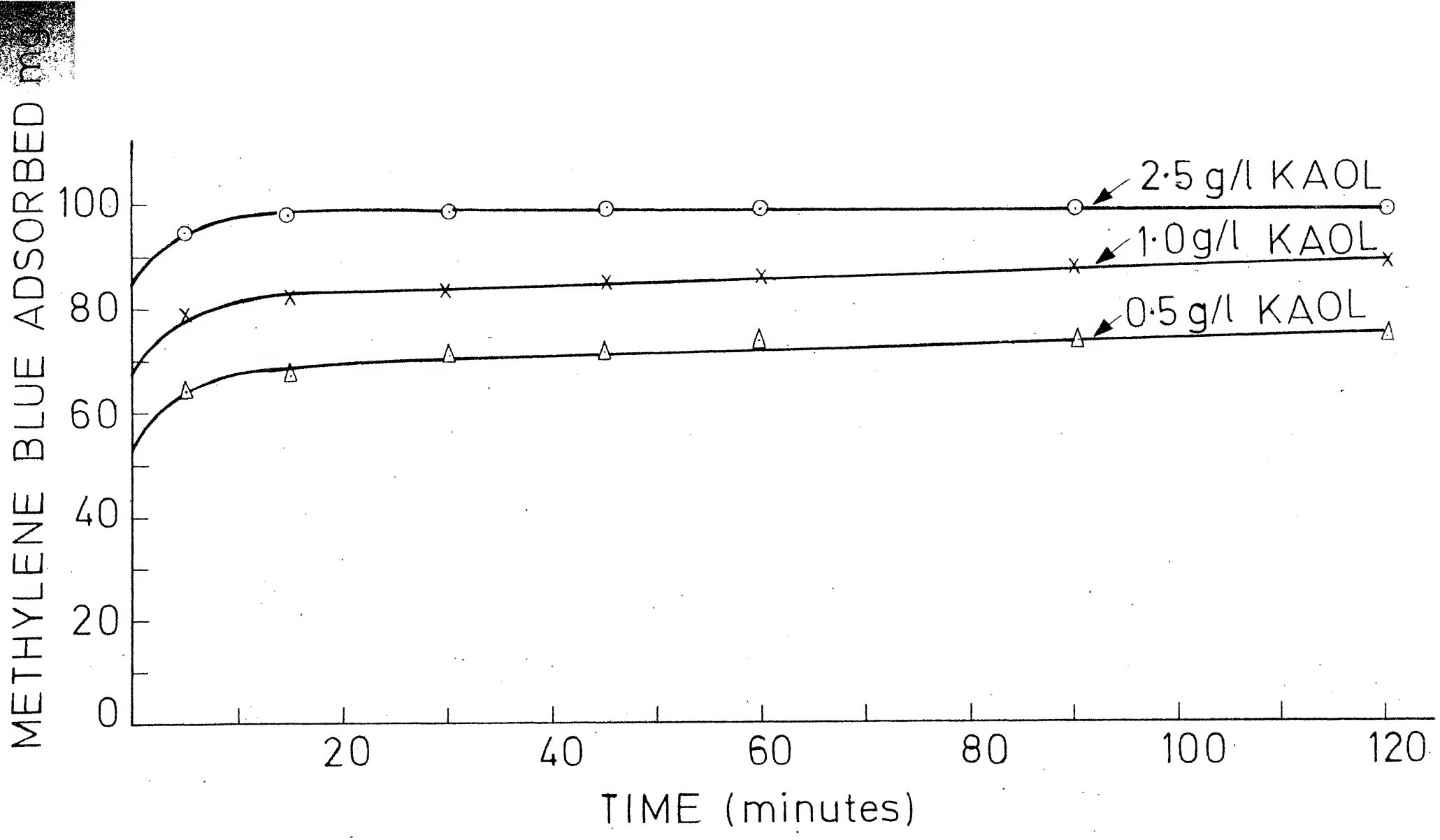


FIG.4 KINETICS OF METHYLENE BLUE ADSORPTION ON KAOLONITE

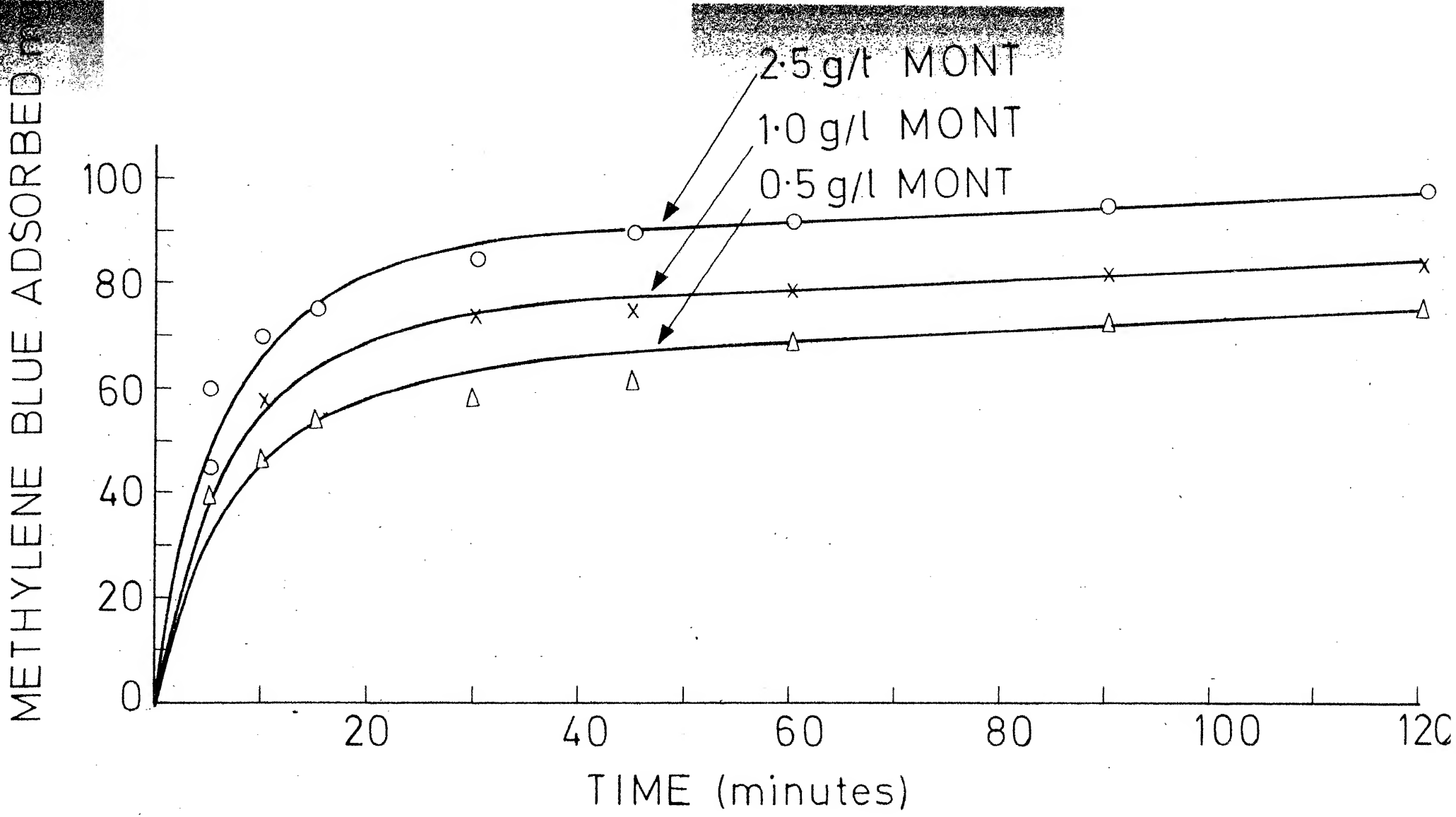


FIG. 5 KINETICS OF METHYLENE BLUE ADSORPTION ON MONTMORILLONITE

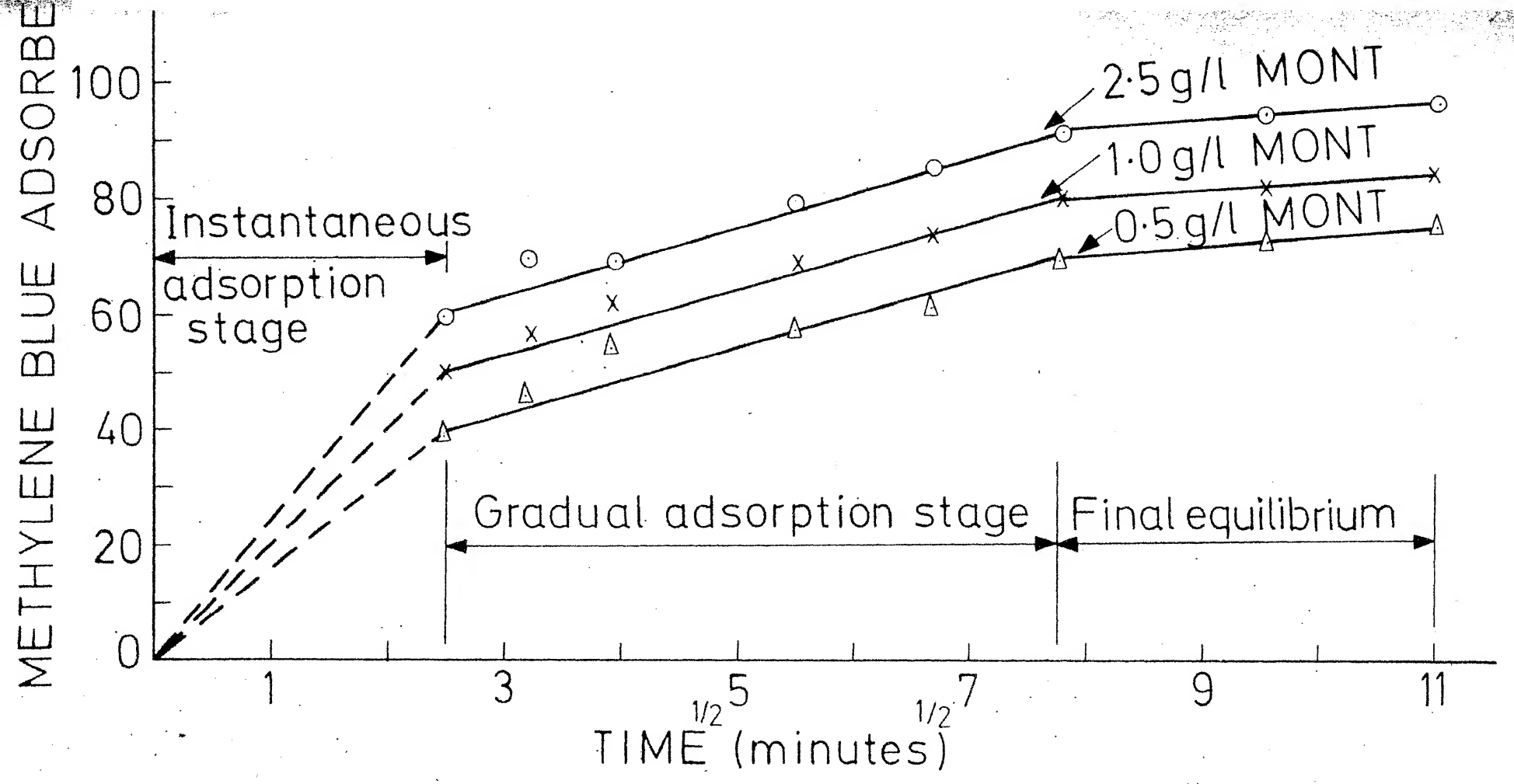


FIG.6 THREE STAGES OF METHYLENE BLUE ADSORPTION ON MONTMORILLONITE

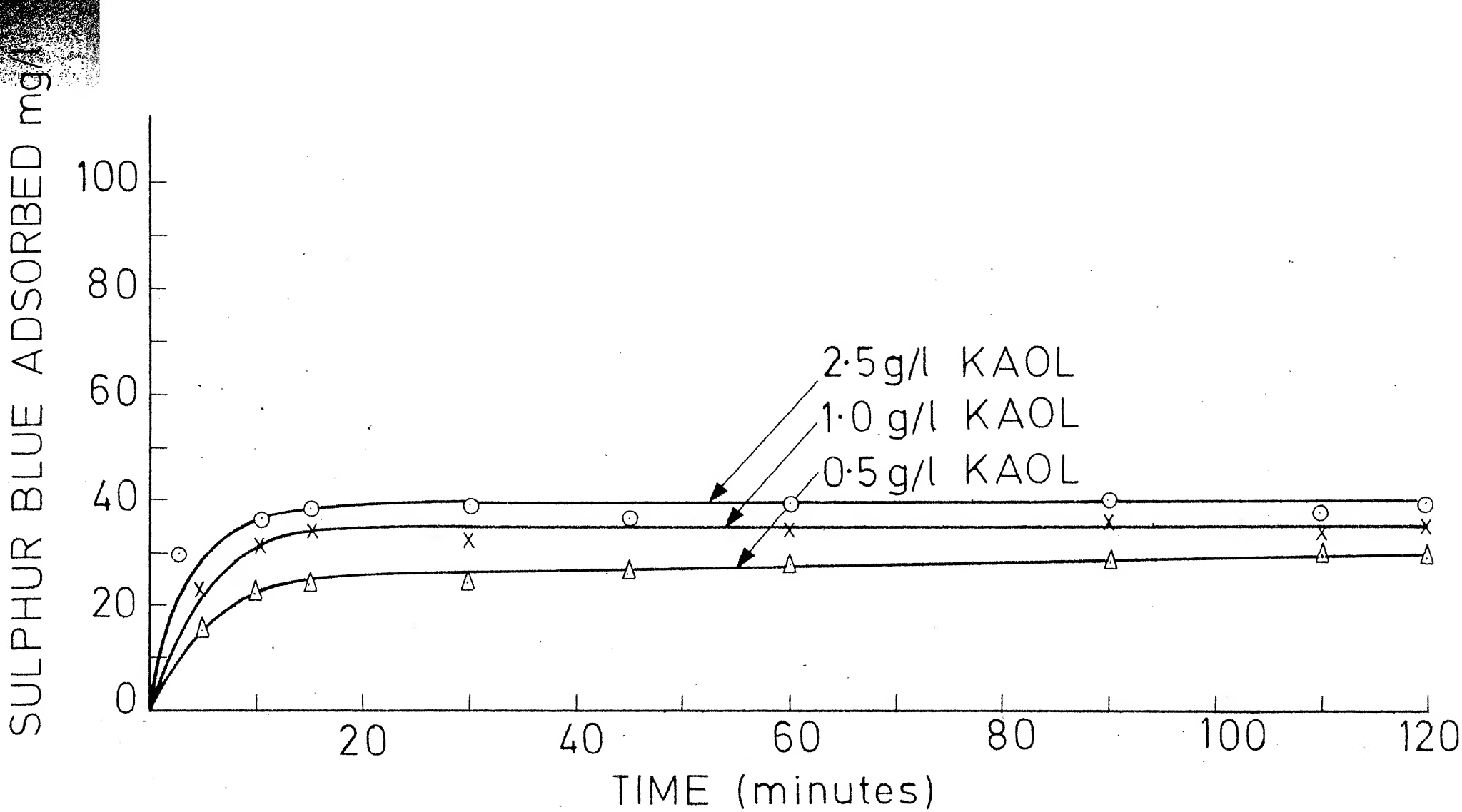


FIG. 7 KINETICS OF SULFUR BLUE ADSORPTION ON KAOLINITE

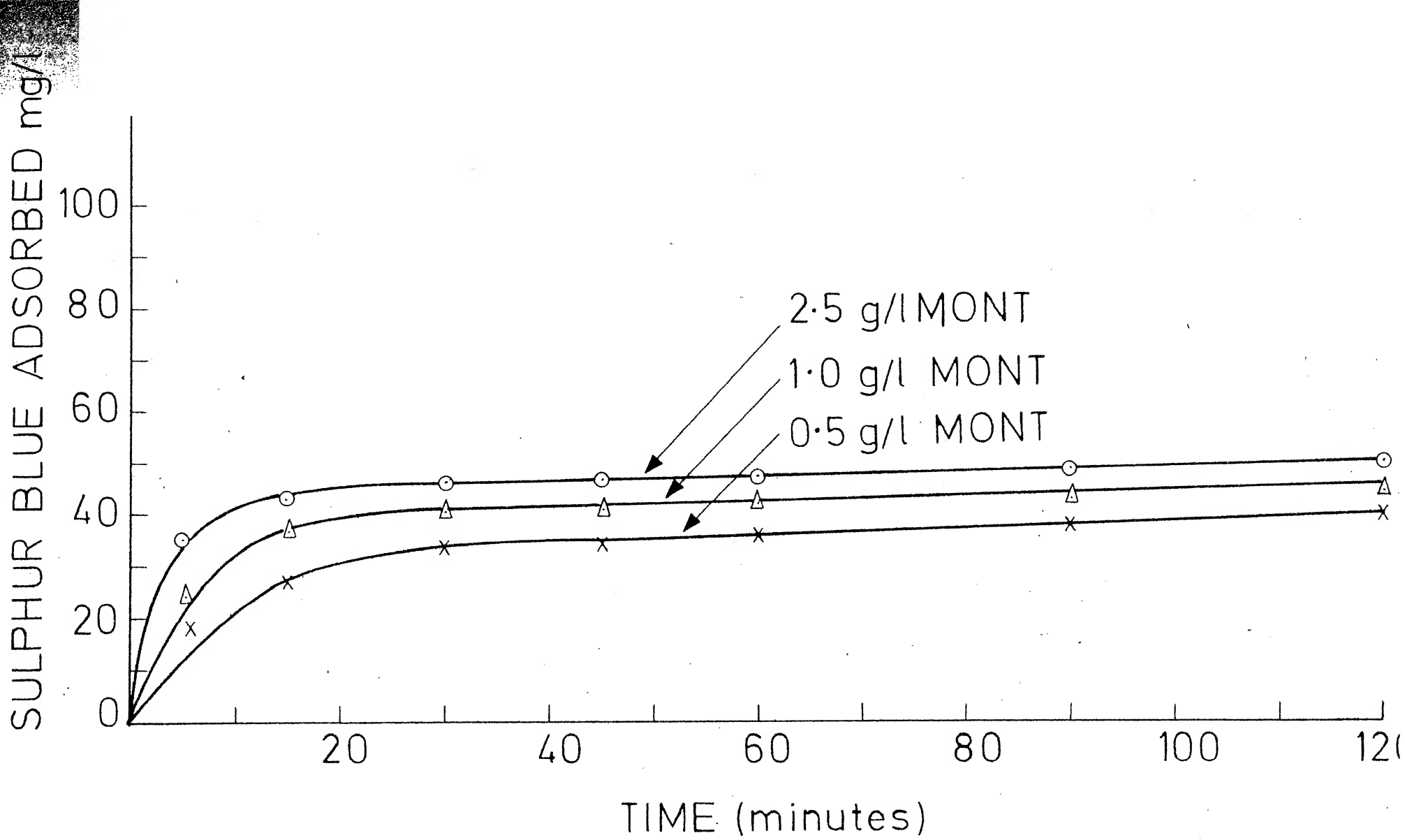


FIG.8 KINETICS OF SULFUR BLUE ADSORPTION ON MONTMORILLONITE

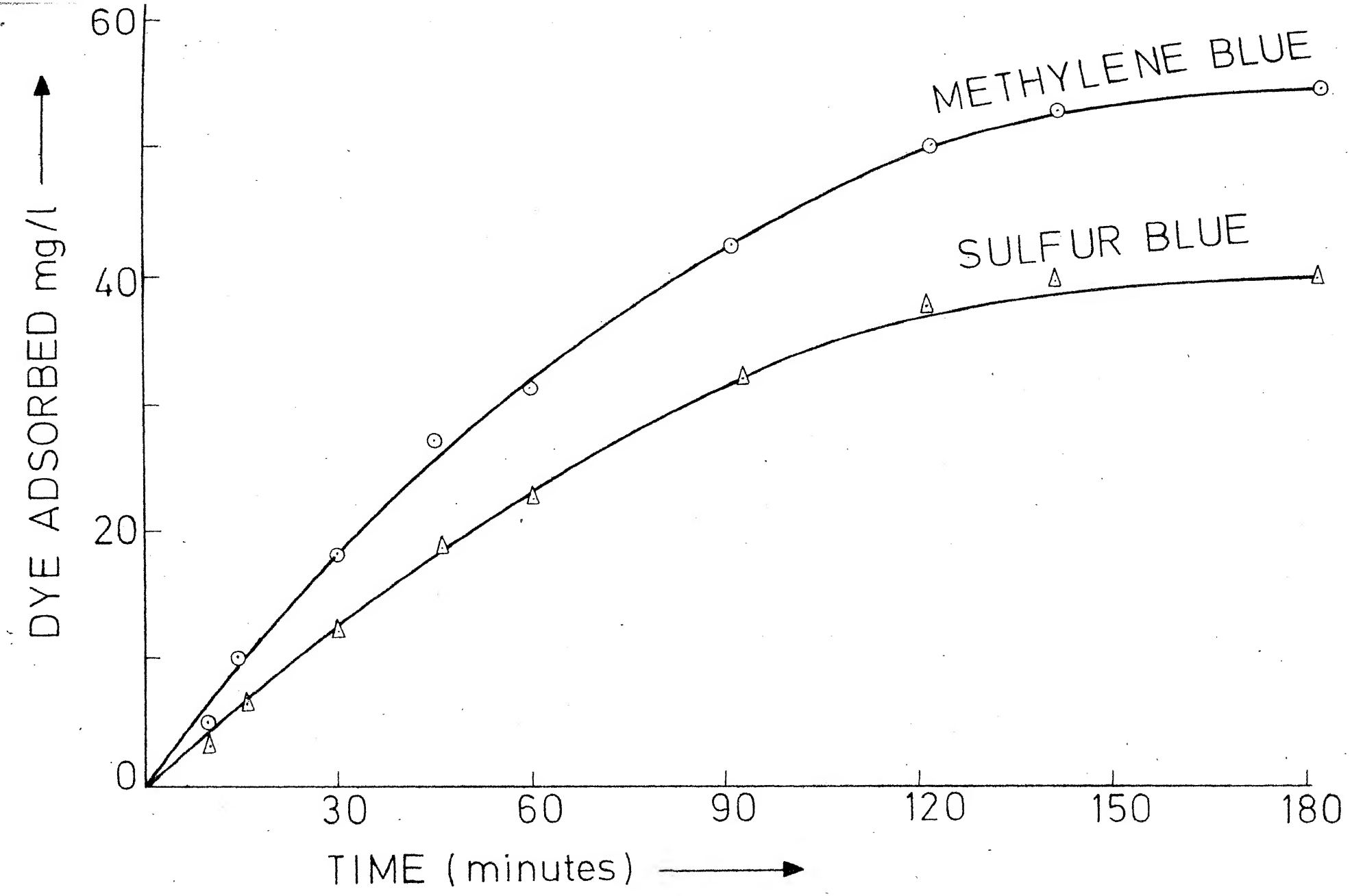


FIG. 9 KINETICS OF DYES ADSORPTION ON ACTIVATED CARBON

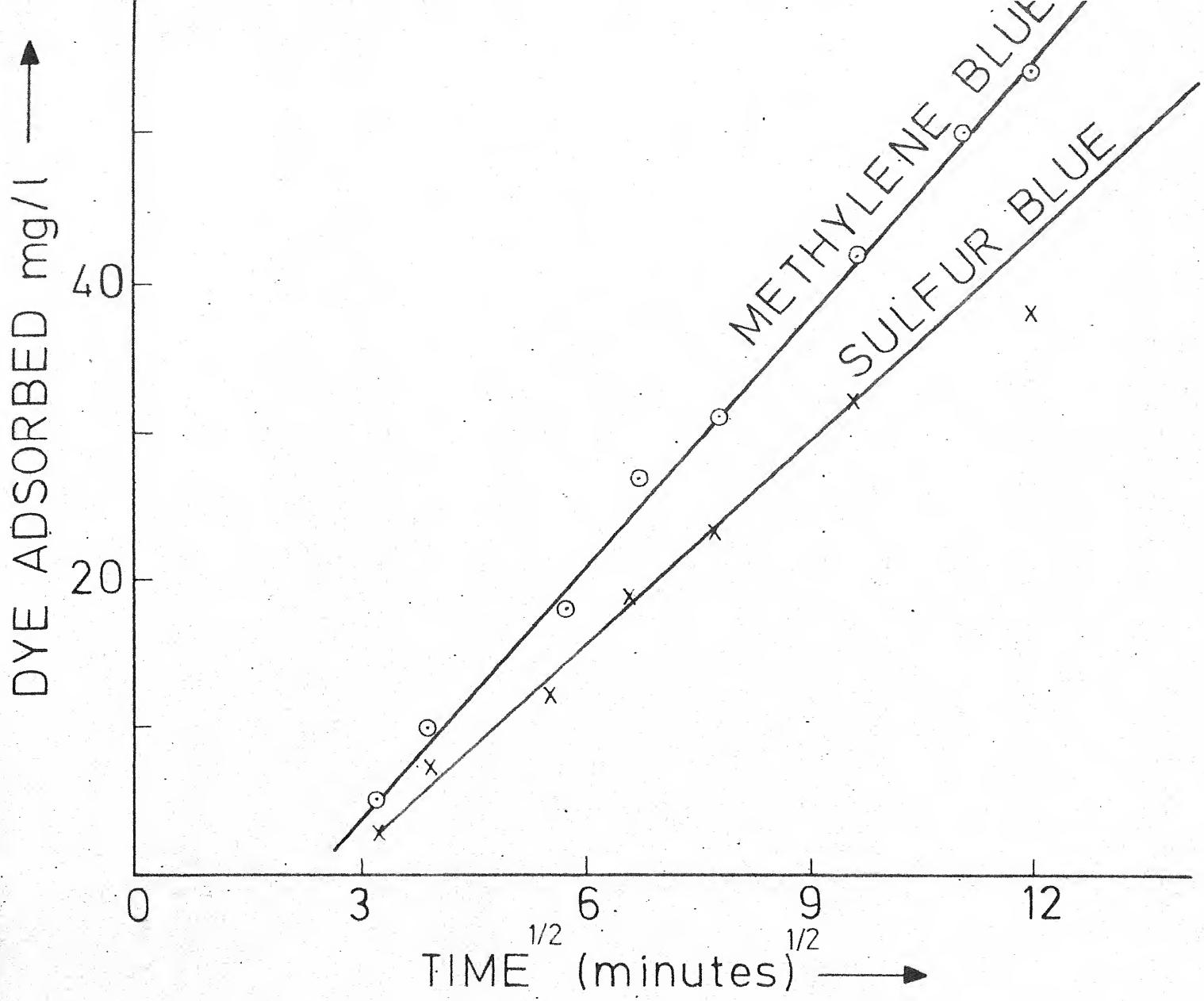


FIG.10 KINETICS OF ADSORPTION OF DYES ON ACT CARBON

(4.1.4) ADSORPTION OF DYES ON ACTIVATED CARBON

The rate of adsorption of both dyes on activated carbon is high initially and almost instantaneous. After about 140 minutes of contact time, the rate slows down and tends to approach a flat plateau. The rate of methylene blue and sulfur blue adsorption on 1 g/l of activated carbon is 0.36 mg/g.min and 0.3 mg/g.min respectively (Fig: 9).

When the amount of dyes adsorbed on granular activated carbon is plotted against square root of time, a linear plot is obtained (Fig. 10) According to Weber and Morris[49] the linearization of the data suggests that the rate of uptake of dyes by activated carbon is governed by the intra particle transport process.

From the rate studies of both dyes on clay minerals and activated carbon, it can be observed that the rate of adsorption of both methylene blue and sulfur blue on clay minerals is faster than that on activated carbon

(4.2) ADSORPTION-DESORPTION STUDIES:

(4.2.1) METHLENE BLUE - CLAY SYSTEMS

The data on the adsorption-desorption studies for methylene blue-clay systems are shown in Table-5. In the case of methylene blue montmorillonite system no desorption was found to occur till the amount of dye adsorbed reached a value 60 meq/100 g., which is the C.E.C of the montmorillonite Hence the adsorption which had taken place till this stage is not reversible and is due to cation exchange taking place between the dye cation and the exchangeable inorganic cation present in the structure of montmorillonite.

The irreversibility of the ion exchange adsorption is probably due to the fact that the organic dye cation which replaces the cations in the clay, makes the clay more hydrophobic (Worrell)[32] and hence do not come out of the clay structure, when resuspended in distilled water, during Desorption experiments.

When the amount of dye added was increased beyond the C.E.C. of the clay, adsorption continued to take place. The portion of the adsorbed dye in excess of the C.E.C. of montmorillonite desorbed readily. The adsorption process continued till the saturation limit of Methylene blue was reached.

These data suggest that the adsorption of Methylene blue on montmorillonite takes place in two stages:

1. Ion Exchange adsorption, which proceeds till the C.E.C. of the clay is reached and is irreversible.

2. Physical Adsorption, which takes place in excess of the C.E.C. and is reversible.

The adsorption of Methylene blue on Kaolinite was also found to follow the above mechanism.

Fig. 11 and 12 are schematic representation of these conclusions, showing that the amount of dye adsorbed is excess over the C.E.C. of both montmorillonite and kaolinite are readily desorbed.

TABLE : 5

ADSORPTION - DESORPTION STUDIES

METHYLENE BLUE - MONTMORILLONITE SYSTEM

1	2	3	4	5	6	7	8	9=(6-8)
ADSORPTION						DESORPTION		
DYE CONCENTRATION ADDED			EQUILIBRIUM DYE CONCN.	AMOUNT OF DYE ADSORBED C_{Ad}		AMOUNT OF DYE DESORVED C_{de}		$C_{Ad}-C_{de}$
mg/l	m.eq / 2.5g	m.eq / 100g	m.eq / 2.5g	m.eq / 2.5g	m.eq / 100g	m.eq / 2.5g	m.eq / 100g	m.eq/100g
100	0.314	15.56	0.002	0.312	12.48	0	0	12.48
200	0.628	25.12	0.013	0.615	24.6	0	0	24.6
300	0.942	37.68	0.022	0.92	36.8	0	0	36.8
400	1.256	50.24	0.056	1.2	48	0	0	48
500	1.57	62.8	0.07	1.5	60	0	0	60
600	1.884	75.36	0.264	1.62	64.8	0.12	4.8	60
750	2.324	92.96	0.624	1.7	68	0.2	8.0	60
1000	3.14	125.6	1.39	1.75	70	0.25	10.0	60
1500	4.71	188.4	2.91	1.8	72	0.3	12.0	60
1900	5.966	238.64	4.166	1.8	72	0.3	12.0	60
METHYLENE BLUE - KAOLONITE SYSTEM								
10	0.0314	1.256	0	0.0314	1.256	0	0	1.256
25	0.0785	3.15	0	0.0785	3.15	0	0	3.15
50	0.157	6.28	0.007	0.15	6.0	0.025	1.0	5.0
75	0.2255	9.2	0.0155	0.21	8.4	0.08	3.2	5.2
100	0.314	12.56	0.004	0.31	12.4	0.185	7.4	5.0
150	0.471	18.84	0.091	0.38	15.2	0.255	10.2	5.0
200	0.628	25.12	0.128	0.5	20	0.375	15.0	5.0
500	1.57	62.8	1.02	0.55	22.0	0.425	17.0	5.0

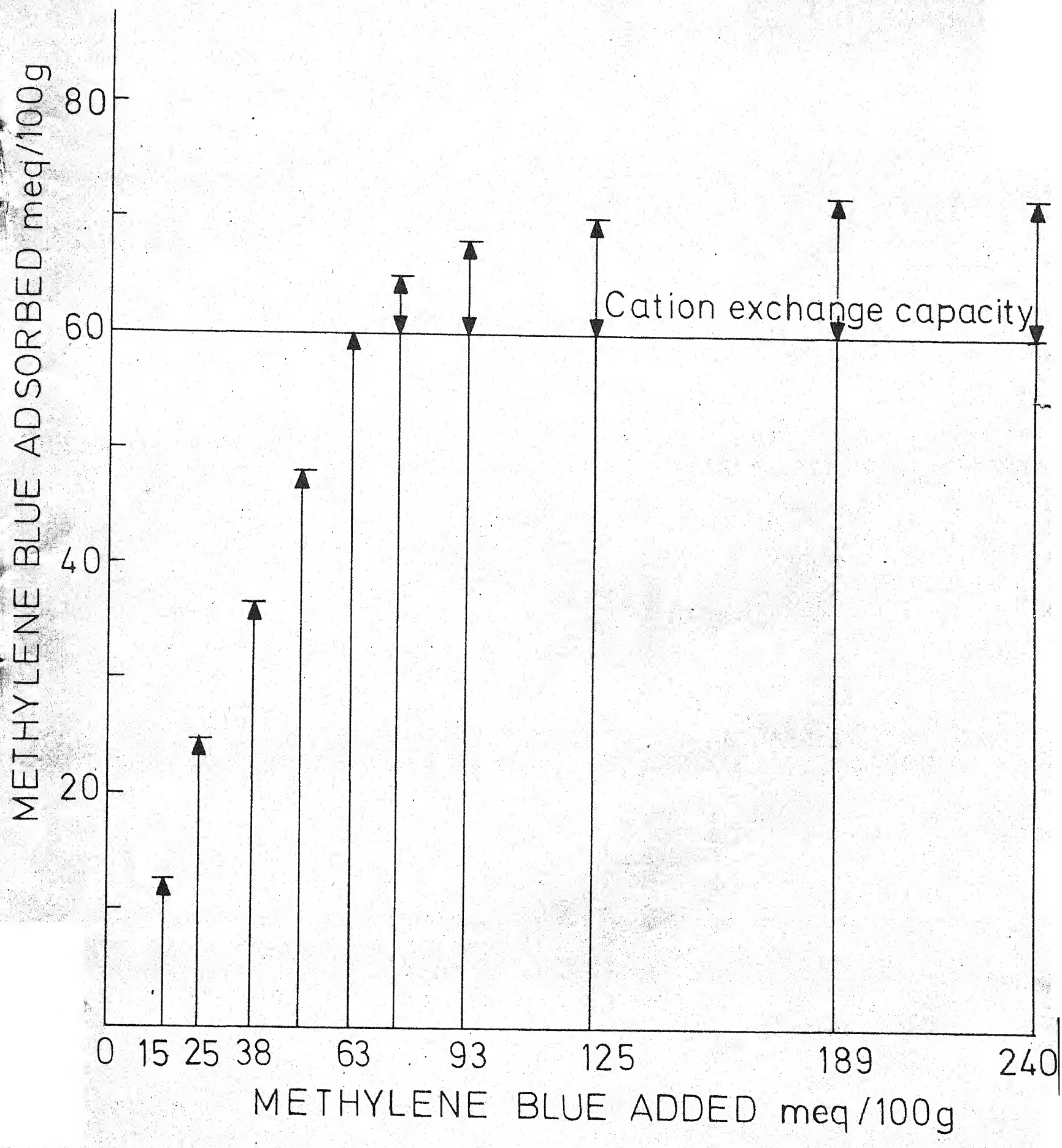


FIG.11 ADSORPTION-DESORPTION OF METHYLENE BLUE-MONT. SYSTEM

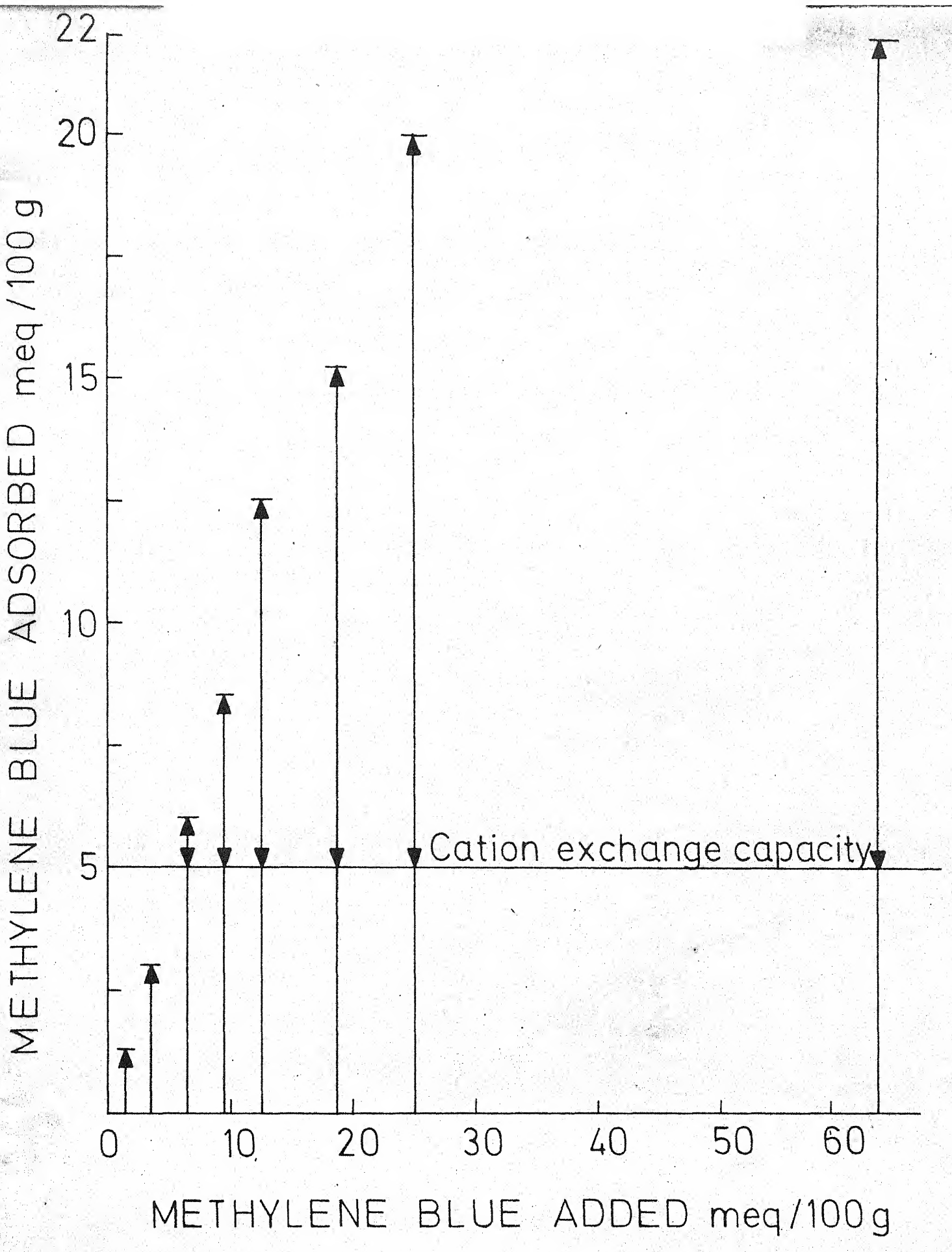


FIG. 12 ADSORPTION-DESORPTION OF METHYLEE BLUE-KAOL SYSTEM

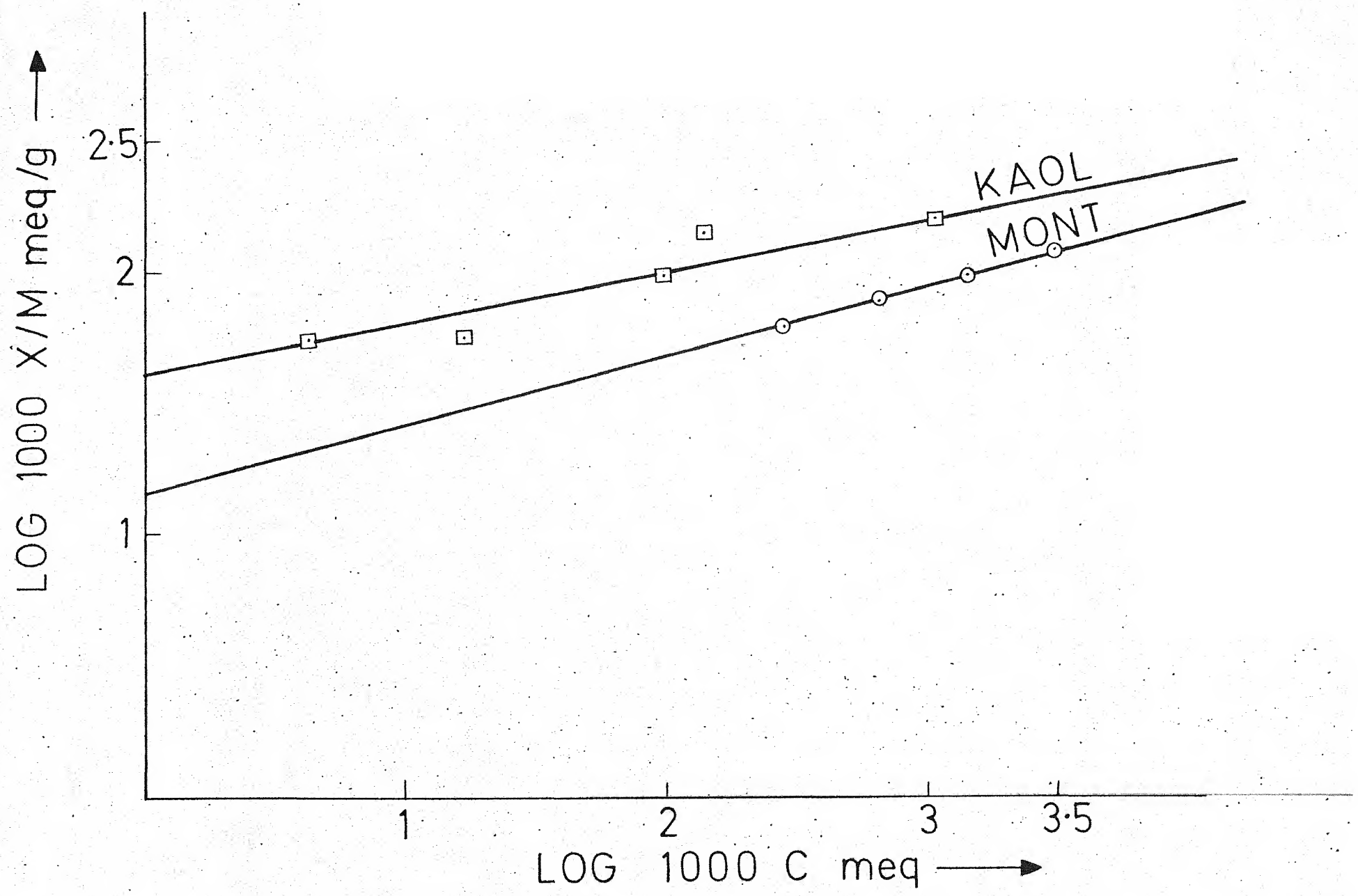


FIG. 13 FREUNDLICH ISOTHERM FOR PHYSICAL ADSORPTION OF METHYLENE BLUE-CLAYS SYSTEMS

The adsorption taking place in excess of the C.E.C. of the clays, is due to the Vanderwaal's force of attraction between the clay particles and the dye molecules. The experimental data for this physical adsorption, follow the Freundlich Isotherm for both the clays (Fig.13). The constants of the Freundlich equation have been found out from the intercept and slope of the fitted straight line on the log-log plott and are given in Appendix 'A'.

For the physical adsorption of Methylene blue-Kaolinite system, Freundlich Isotherm is of the form,

$$\frac{X}{M} = 4.16 \; C^{0.188} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where , X/M = Amount of dye adsorbed per unit weight of clay in m.eq/g.

C = Equlibrium dye concentration in m.eq

For Methylene blue - Montmorillonite, it is of the form,

$$\frac{X}{M} = 14.15 \; C^{0.253} \quad \ldots\ldots\ldots \quad (2)$$

The Total adsorption process for Methylene blue- Clay systems can be written as ,

Total adsorption = Ion exchange adsorption + Physical adsorption.

For Methylene blue - Kaolinite system ,

$$\frac{X}{M} = 5 \; \frac{m.eq}{100g} + 41.6 \; C^{0.188} \quad \ldots\ldots \quad (3)$$

For Methylene blue - Montmorillonite system,

$$\frac{X}{M} = 60 \frac{m.eq}{100g} + 14.15 \; C^{0.253} \quad \ldots\ldots\ldots \quad (4)$$

In the Ion exchange adsorption the amount of dye adsorbed, is independent of the dye concentration in solution and is proportional only to the quantity of clay present. Physical adsorption depends on the concentration of dye remaining in solution at equlibrium.

(4.2.1.1) X-RAY OBSERVATIONS

X-ray diffraction patterns of the untreated clay samples and also after adsorption-desorption studies were taken with the help of GE-XRD X-ray Diffractometer, with Copper k α radiation.

The basal spacing of the untreated Kaolinite is 7.13 Å. After adsorption it is 7.3 A° and after desorption , 7.24 A° (Fig.14). There is practically no difference in the above three values. These data suggest that the adsorption of Methylene blue on Kaolinite can be considered to be limited only to the exterior surface of Kaolinite. Illite which was present as an impurity in the Kaolinite sample also showed the same behaviour, with very little changes in the basal spacing for all the three types of observations.

The basal spacing of untreated montmorillonite is 15.76 A° and this peak is quite sharp. After adsorption, the sharpness and length of the peak reduced appreciably and the peak

widened, which suggested that some change is taking place in the structure of montmorillonite .(Fig.15). There is a doubtful peak at 24.5 A° which may or may not imply that the adsorbed dye cations enter the interlayer of montmorillonite and increase the basal spacing, However, the montmorillonite occurring as an impurity in the Kaolinite sample , showed a slight increase in basal spacing, after adsorption. The d-spacing of montmorillonite present in the Kaolinite sample is 15.22 A° and after adsorption it is 16.35 A°. These data suggest that adsorption takes place in the interlayer between unit layers of montmorillonite, causing the clay to expand.

(4.2.1.2) DIFFERENTIAL THERMAL ANALYSIS (D.T.A.) DATA.

Thermal analysis of untreated montmorillonite and Methylene blue-montmorillonite complex after adsorption was carried out with the help of DU-PONT-900 Thermal Analyser. The rate of heating was maintained at 20°C/min. The thermograms are shown in Fig.16.

The Methylene blue-montmorillonite complex showed a characteristic exothermic peak at 595°C, which was not present in the untreated clay sample. This observation is in close agreement with the results of Ramachandran[41] who observed an exothermic peak for the same system at 600°C. He also reported that, from D.T.A data and thermogravimetric analysis, this peak occurred due to the

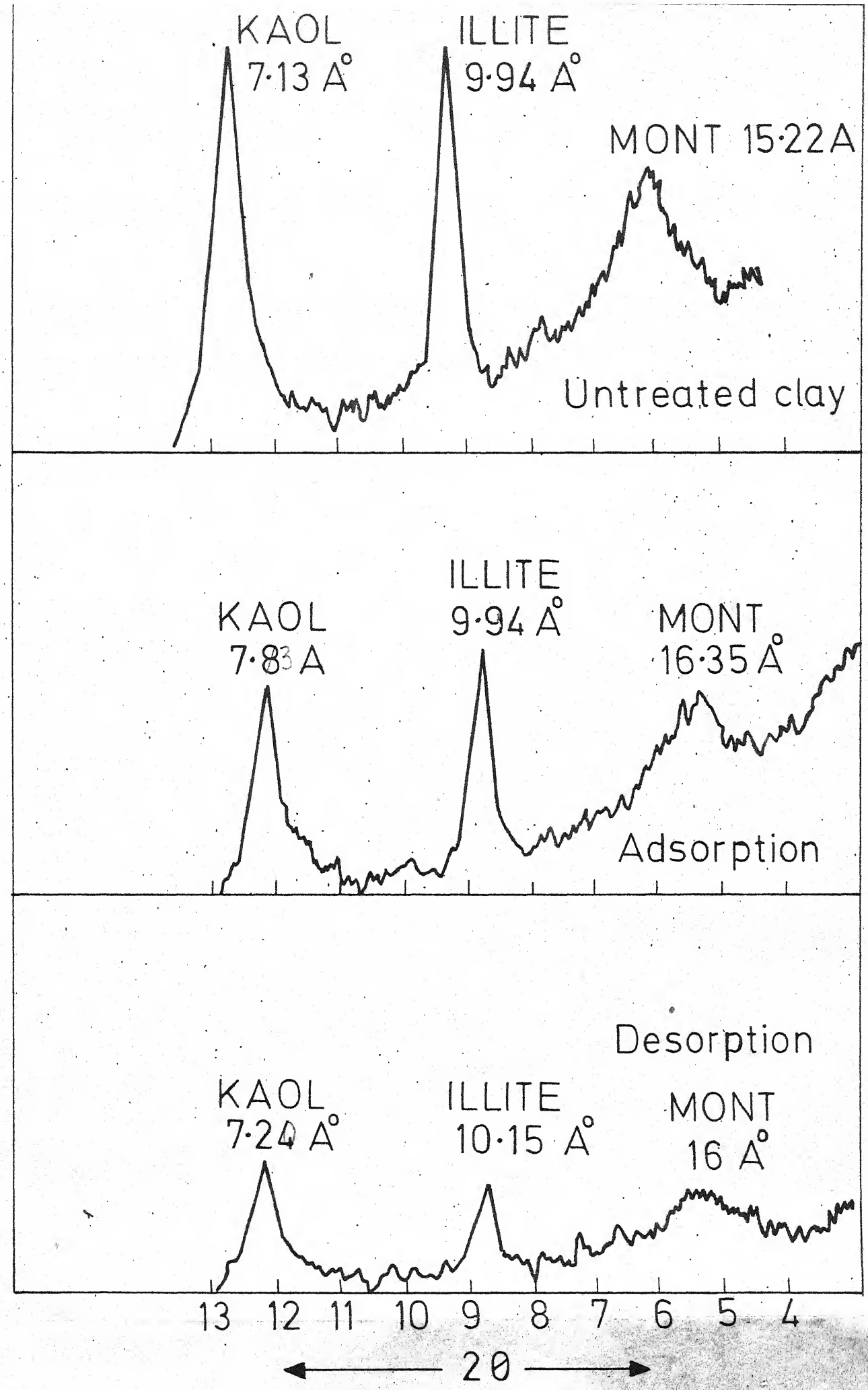


FIG. 14 X-RAY OBSERVATIONS ON METHYLENE BLUE-KAOL SYS

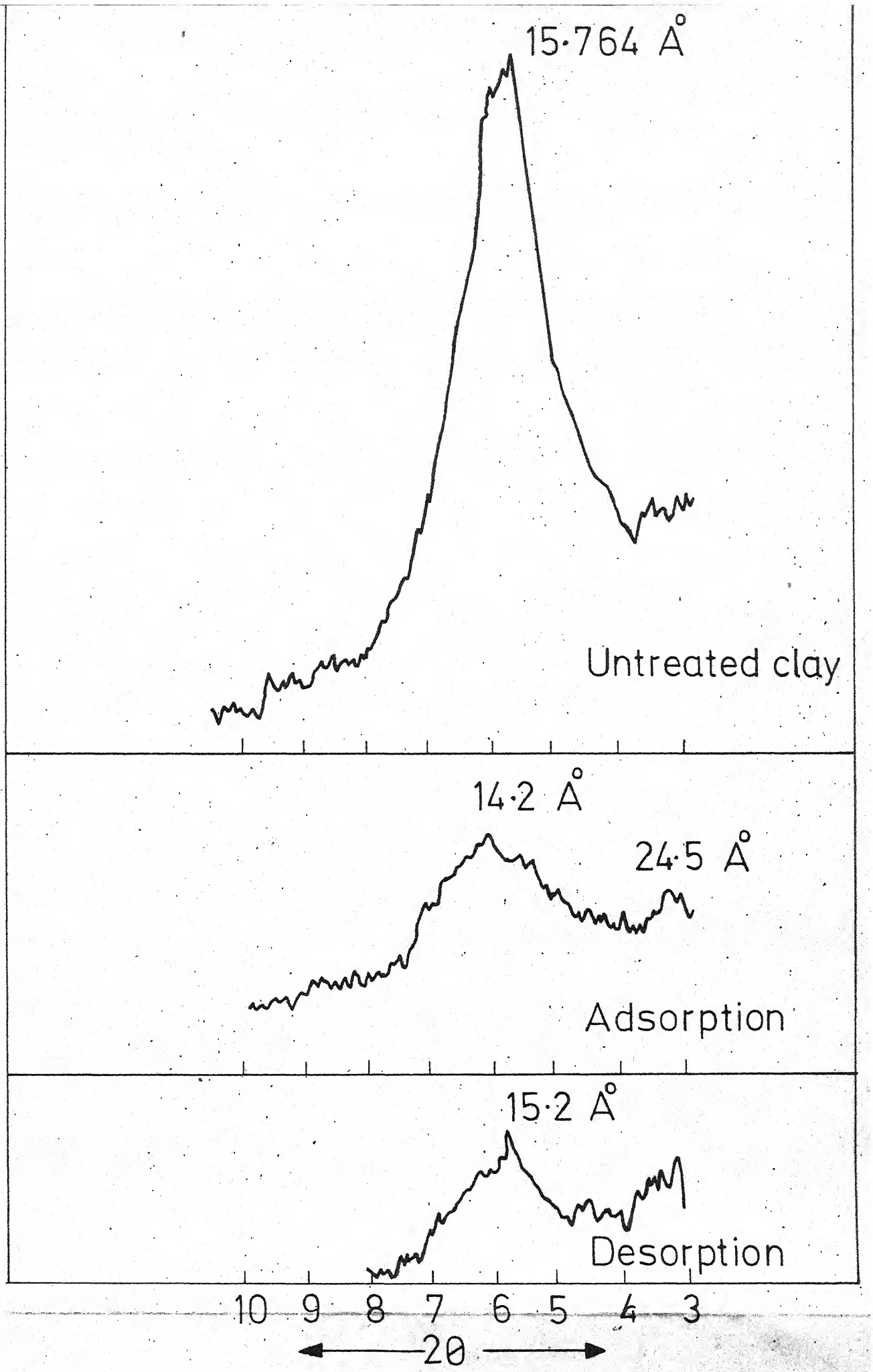
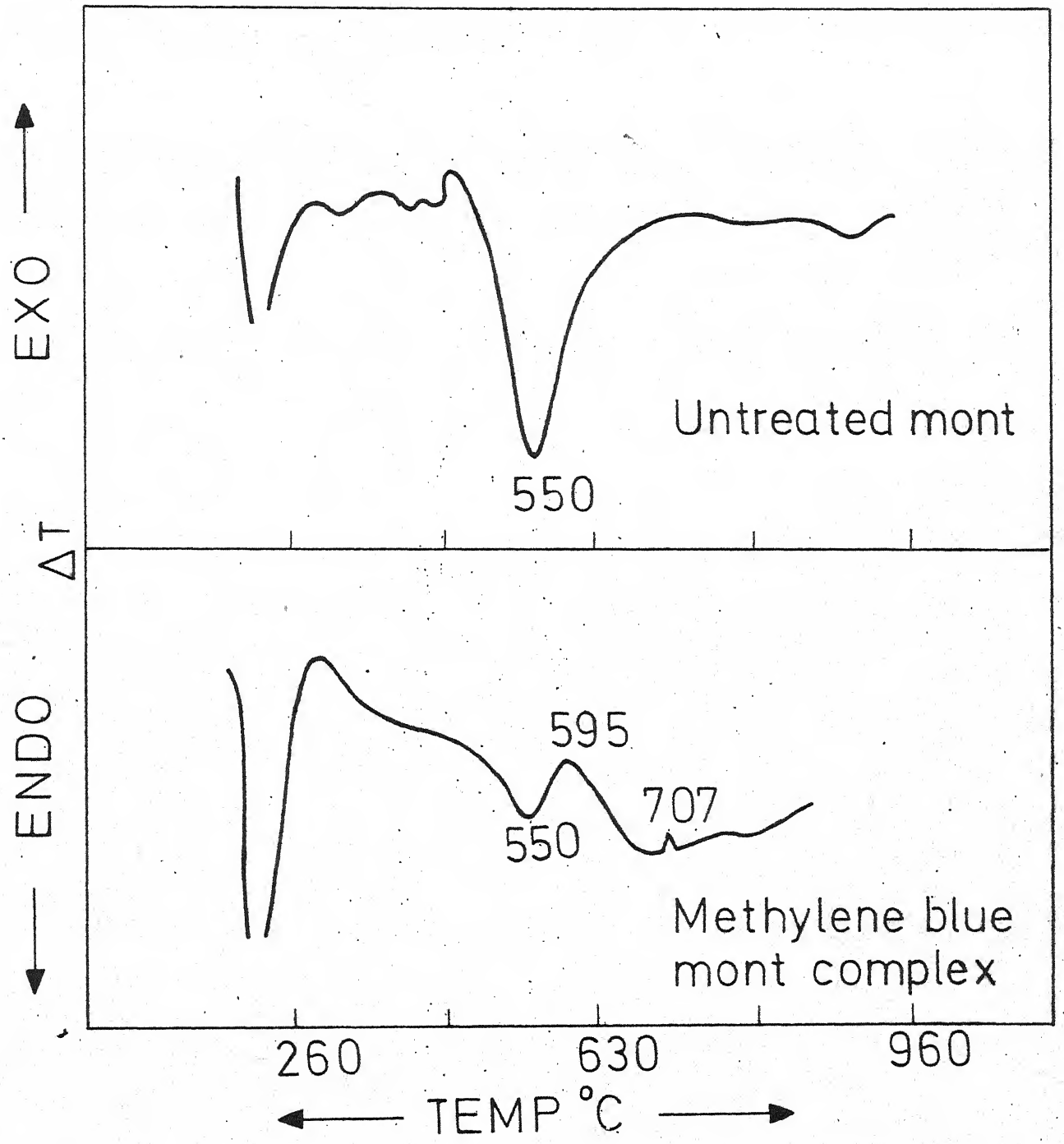


FIG. 15 X-RAY OBSERVATIONS OF METHYLENE-BLUE MONT.



I. I. T. KANPUR
CENTRAL LIBRARY
Acc. A 26205

FIG. 16 D.T.A. OF METHYLENE BLUE-MONT SYSTEM

oxidation of the dye present in the interlayer of montmorillonite. Thus interlayer adsorption of Methylene blue on montmorillonite is confirmed by D.T.A. There is another exothermic peak at 707°C , characteristic of the Methylene blue - montmorillonite complex but is less intense than the peak at 595°C. The endothermic peak at 550°C characteristic of montmorillonite occurred in both untreated clay and Methylene blue adsorbed clay.

(4.2.2) SULFUR BLUE - CLAY SYSTEMS.

The amount of Sulfur blue adsorbed on both the clay minerals is very low as compared with Methylene blue adsorption. The maximum amount of Sulfur blue dye adsorbed in the case of Kaolinite is 5.248 m.eq/100g as compared with that of Methylene blue - Kaolinite of 22 m.eq/100g. The corresponding values for Sulfur blue - montmorillonite is 6.56 m.eq/100g as compared with that of Methylene blue-montmorillonite of 72 m.eq/100 g. The low values of Sulfur blue adsorption on clays is due to the fact that Sulfur blue is an anionic dye and the adsorption is due to Anion exchange taking place between the dye anion and the inorganic anions present in clays. The anion exchange capacity (A.E.C) of Kaolinite and montmorillonite have been reported as 6 and 8 m.eq/100g respectively[20]. In the case of Kaolinite, the amount of dye adsorbed almost reached the A.E.C value. For montmorillonite, about 75% of the A.E.C was reached before adsorption

ceased to occur. For both clays no desorption was found to occur, suggesting that the total adsorption process comprises of only Anion exchange with no contribution of Physical adsorption.

(4.2.3) EFFECT OF P^H ON ADSORPTION

The effect of P^H of the dye solution on adsorption was studied by varying the P^H of the aqueous system with 1N NaOH. It was found that the adsorption of Methylene blue increased, with increase in P^H. Faruqi[26] showed that this increase in adsorption is due to the change in the charge distribution on the exposed surfaces of the clays, when the P^H of the bulk phase is increased. Initially only the basal pinacoid surfaces are negatively charged, while the edges have positive charge. In the alkaline range of P^H, the edges also become negatively charged by the substitution of OH^- ions into the structure, thus attracting more dye cations and increasing the adsorption. This behaviour was observed for Methylene blue adsorption on both clays. (Fig.17). Sulfur blue clays systems did not show any increase in adsorption , as the mechanism of adsorption is apparently through Anion exchange and hence increased negative surface does not make any difference.

(4.2.4) ADSORPTION ON ACTIVATED CARBON

The adsorption of Methylene blue and Sulfur blue, on Activated carbon proceeded slowly after an initial high rate . The final equilibrium was reached after about 7 days. On the first day, the test

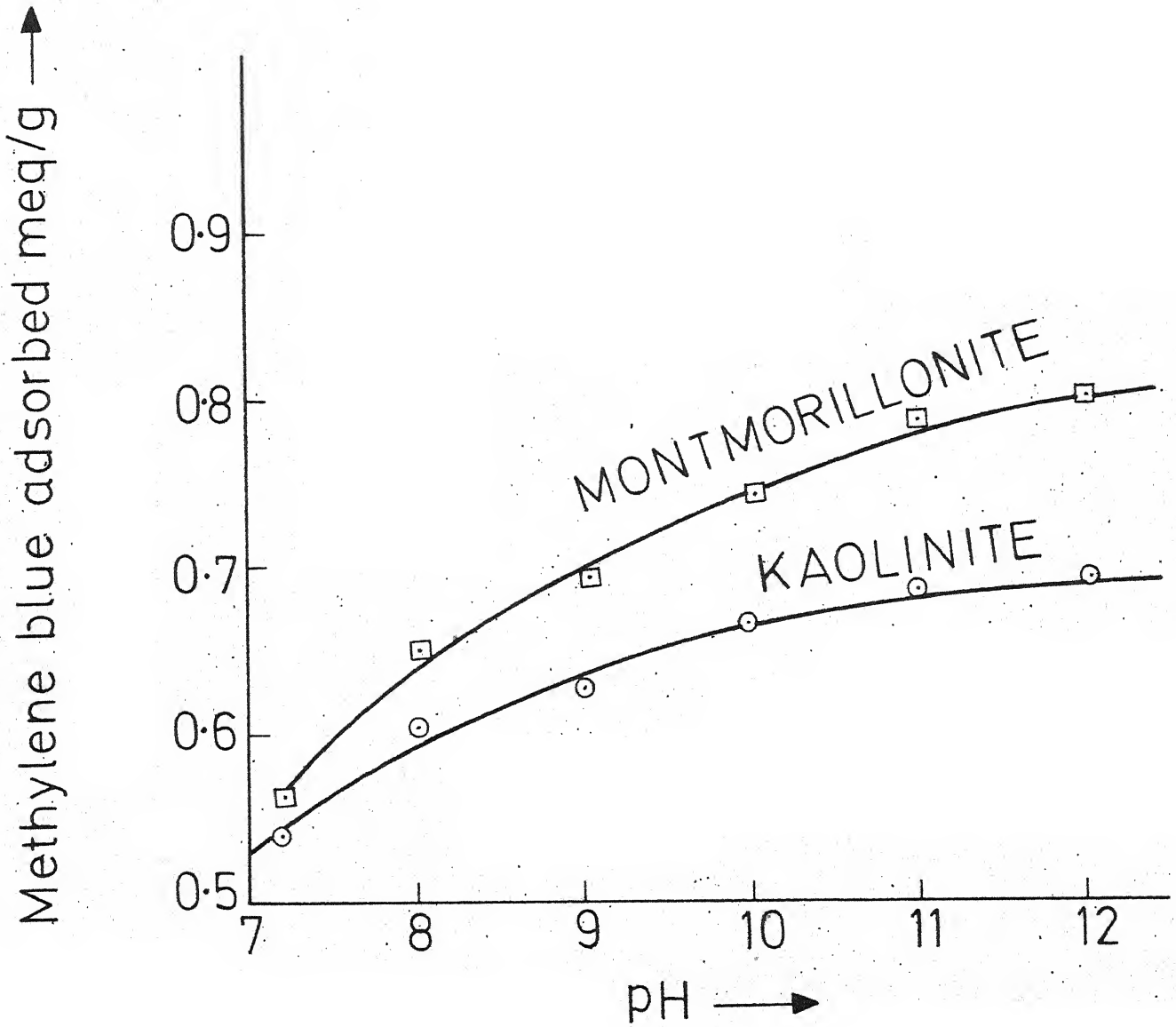


FIG. 17 EFFECT OF pH ON METHYLENE BLUE-CLAYS SYSTEMS

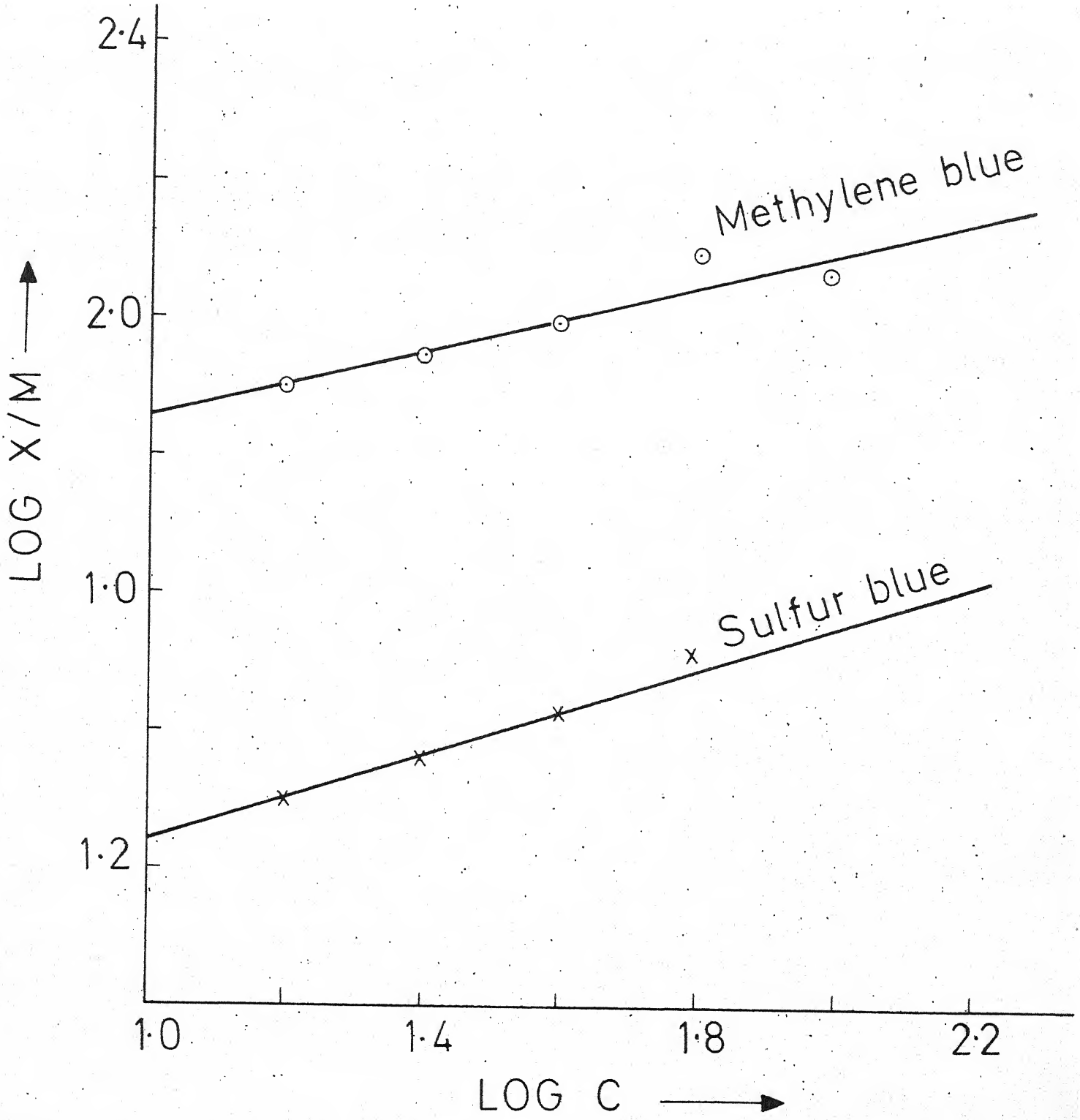


FIG. 18 FREUNDLICH ISOTHERM FOR ADSORPTION OF DYES ON ACT. CARBON

solutions were almost continuously agitated and afterwards it was allowed to standstill till the system equlibrated. The slow attainment of equlibrium is due to the granularity of Activated carbon and the diffusion of dye molecules through macro and micro pores of carbon.

Methylene blue was adsorbed more easily and in larger quantities than Sulfur blue. The probable reasons for this behaviour are as follows:

1. The molecular weight of Methylene blue is 320 which is more than that of Sulfur blue 305. It has been established that adsorption increase with increase in the molecular weight of the adsorbate.

2. The solubility of Methylene blue, 1.9g/l , is less than that of Sulfur blue, 3.2g/l in water. The lower solubility of Methylene blue in water means that it is more hydrophobic in nature than Sulfur blue and hence has greater affinity for the solid phase. On the contrary, Sulfur blue has a greater affinity for the Aqueous phase and comparatively less affinity towards carbon.

3. The Methylene blue is positively charged and hence is easily attracted by the negatively charged surface of carbon. Surfur blue is a negatively charged dye and hence is less attracted by the carbon surface.

The adsorption of both dyes on activated carbon follow the Freundlich Isotherm. (Fig.18).

For Methylene blue- activated carbon system, the Freundlich isotherm is of the form $\frac{X}{M} = 72.5\ C^{0.2}$.

For Sulfur blue - activated carbon, it is of the form ,

$$\frac{X}{M} = 17.35\ C^{0.33}$$

The experimental data and the constants of the Freundlich equation are given in Appendix 'B'

No desorption was found to occur for both Methylene blue and Sulfur blue - activated carbon systems at room temperature. This suggests that chemical bonding takes place between the adsorbed dye molecules and the carbon surface, indicating chemisorption.

(4.3) COMPARISON OF THE ADSORPTION CAPACITIES OF CLAYMINERALS AND ACTIVATED CARBON

The adsorption capacity of Kaolinite, Montmorillonite and activated carbon for Methylene blue are 0.22 m.eq/g, 0.72 m.eq/g and 0.21 m.eq/g. From this data , it can be seen that montonorillonite has the highest adsorption capacity for Methylene blue. Kaolinite and activated carbon have almost same adsorption capacities. In view of the low cost of Kaolinite it can be preferred over the costly activated carbon.

The analysis of the Sulfur blue dye waste is shown in Table : 6

TABLE : 6 ANALYSIS OF SULFUR BLUE DYE WASTE

P^H	=	11.2
Colour concentration	=	1020 mg/l
Alkalinity	=	6020 mg/l as $CaCO_3$
Total Solids	=	5025 mg/l
Suspended Solids	=	3200 mg/l
Dissolved Solids	=	1800 mg/l

The dye waste was diluted to 100 mg/l by distilled water and was then treated by clay minerals, activated carbon and lime. The percent of colour removal of the dye waste by the above four materials are given in Table: 7

TABLE: 7 PERCENT COLOUR REMOVAL OF SULFUR BLUE DYE WASTE BY VARIOUS MATERIALS

PROCESS	MATERIAL	AMOUNT OF MATERIAL g/l	PERCENT COLOUR REMOVAL
ADSORPTION	Kaolinite	2.5	42
	Montmorillonite	2.5	50
	Activated Carbon	2.5	48
COAGULATION	Lime	0.05	94

(4.6) SIGNIFICANCE OF ADSORPTION-DESORPTION DATA IN STREAM POLLUTION STUDIES

The conclusions of the experiments described above that clay minerals can adsorb increasing amounts of cationic dyes over and above their Cation Exchange capacity and that this excess amount is readily desorbed in distilled water, lead to some interesting speculations. It is well known that clays like Kaolinite and montmorillonite form the bulk of the suspended load in rivers and also are important constituents of the bottom sediments. The dye waste entering a river has, therefore, ample opportunity to come in contact with these clay minerals. As the dye concentration increases, the clays would remove colour first by irreversible chemical adsorption and then by reversible physical adsorption when the C.E.C. is exceeded. Under normal circumstances one expects that the clays would hold considerable amounts of dye on their surface by physical adsorption. This amount would, however, be released back into the river water once the amount of water increases for example, during floods. The situation would be similar to putting the clay minerals with the physically adsorbed dyes into a more dilute medium.

This means, therefore, that the bottom sediments and the suspended load can periodically "self pollute" the river water although the input of the dye may remain constant.

(4.7) SUGGESTIONS FOR FUTURE STUDY

1. Study of the effect of orientation and size of the dye molecule on the effeciency of adsorption by clay minerals.

2. Pilot plant studies on the adsorption of Basic dyes on clay minerals to evaluate the design parameters for treatment units for colour removal.

3. Recovery of dyes from dye wastes after adsorption on clay minerals.

CHAPTER: V

CONCLUSIONS:

On the basis of the present study, the following conclusions have been drawn:

1. The rate study revealed that adsorption of methylene blue on kaolinite was nearly instantaneous and that on montmorillonite was rapid initially and slowed down gradually before reaching equilibrium, suggesting interlayer transport of the dye molecule. Intra particle transport was found to be the rate limiting step in the case of both methylene blue and sulfur blue adsorption on granular activated carbon.

2. Adsorption - Desorption studies of Methylene blue - clay systems revealed that the adsorption of this dye on both clays occurs in two stages:

(1) Cation exchange adsorption, till the CEC of the clays is reached and is irreversible.

(2) Physical adsorption, in excess of CEC of clays, which was reversible and followed Freundlich Isotherm. The dye adsorbed in excess of CEC completely desorbed for both clays.

3. X-ray observations of Methylene blue clay complexs showed that the adsorption on kaolinite occurs only on the surface with no change in the basal spacing of the clay after adsorption and desorption. The adsorption on montmorillonite suggested the entry of dye cations into the interlayer. The change in clay structure due to this adsorption was apparently not drastic enough to produce a detectable shift of X-ray peak position.

The sharpness and the height of the peaks however went through an unmistakeable reduction.

4. Differential thermal analysis of Methylene blue-montmorillonite complex conclusively proved the presence of dye molecules in the interlayer which are oxidized around 595°C giving a characteristic exothermic peak.

5. The adsorption of sulfur blue on both clays is due to Anion exchange. No desorption was found to occur, suggesting that the anion exchange adsorption is irreversible. The amount of sulfur blue dye adsorbed is less than that of Methylene blue for both clays and activated carbon.

6. Increase in pH of the aqueous solution increased the adsorption of Methylene blue on both clay minerals. Sulfur blue did not show such a behaviour.

7. The adsorption of both dyes on activated carbon followed Freundlich Isotherm. No desorption of the dyes was found to occur indicating chemisorption of the dyes on activated carbon.

8. Montmorillonite showed the highest adsorbing capacity for Methylene blue Kaolinite and activated carbon have more or less same adsorbing capacity.

9. The adsorbing capacity of both the clay minerals and activated carbon was almost same for sulfur blue.

10. Adsorption on clay minerals and activated carbon removed the colour of sulfur blue dye waste by about 42 - 50 % and coagulation by lime removed 94 % of colour.

11. The results of the adsorption-desorption studies of Methylene blue on clay minerals were extended to the natural water bodies. The possibility of self pollution of the stream by desorption of dye from clay surfaces during floods was outlined.

CHAPTER : VI

REFERENCES

1. Souther, R.H. and T.A. Alspaugh. Textile Waste Treatment Studies. Proc. 13th Ind. Waste Conference, Purdue Univ. pp: 662, (1958).
2. McKee, J.L. Water Quality Criteria , A.W.W.A. Pub., Inc , New York, pp: 55, (1963).
3. Souther, R.H. and T.A. Alspaugh. Biological Treatment of Mixtures of Textile Wastes and Domestic Sewage. Sewage and Ind. Wastes , 28: 166, (1956).
4. McCarthy, J.A. The Textile Industry and Stream Pollution. Am.Dyestuff Reporter , 39: 732, (1950).
5. Nemerov, N.L. Colour and Methods of Colour Removal. Proc. 11th Ind. Waste Conference, Purdue Univ. pp: 584, (1956).
6. Porges, R., R.K.Horton and H.B.Gotaas. Chemical precipitation of Sulfur Dye Wastes on a Pilot Plant Scale. Sewage Works J. , 13: 308, (1941).
7. Smallhorst, D.F. Textile Waste Treatment in Texas. Am.Dyestuff Reporter , 44: 386 (1955).
8. Souther, R.H. and T.A. Alspaugh. Biological Treatment of Mixtures of Highly Alkaline Textile - Mill Waste and Sewage. Am. Dyestuff Reporter, 44: 390 (1955).
9. Geyer, J.C. Textile Industry. Ind. Engg. Chemistry, 39:653 (1947).
10. Beach, C.J. and M.G. Beach. Treatment of Alkaline Dye Wastes with Flue Gas. Proc. 5th Southern Municipal and Ind.Waste Conference. pp: 162, (1956).

11. Thornton, H.A. and J.R. Moore. Adsorbents in Waste Water Treatment - Dye Adsorption and Recovery Studies. Sewage and Ind. Wastes, 23: 497, (1951).

12. Shell, F.D. Treatment of Trade Waste with Activated Carbon. Sewage Works J. , 7: 946, (1935).

13. Mudri, S.S. et al. Treatment of Wastes from a Dye Factory. Environmental Health , 12: 201 , (1970).

14. Rak, M. Treating Waste Water from Organic-Dye Manufacture. Czech, 105: 798, (1962). (Chem. Abs. 59, 13684, 1963).

15. Ragan, J.L. and R.H. Maurer. Industrial Waste Disposal by Solar Evaporation. Industrial Water and Wastes , 8: 37, (1963).

16. Michelson, D.L. Treatment of Dye Wastes, Text. Chem. Color, 1:179,(1969). (Chem. Abs. 72: 103498, 1970).

17. Todd, D.B. and C.A. Hopper, Centrifugal Extraction of Dyes. Chem. Engg. Progress , 67:60 , (1971).

18. Williamson, R. Handling Dye Wastes in a Municipal Plant. Pub. Works, 102: 58 , (1971).

19. Aurich, C. et al . Treatment of Textile Dyeing Wastes by Dynamically Formed Membranes. J. W.P.C.F , 44: 1545, (1972).

20. Grim, R.E. Clay Mineralogy, McGraw-Hill, New York, pp: 44, 129,(1968).

21. Hunter, R.J. and A.E. Alexander. Surface Properties and Flow Behaviour of Kaolinite. J. Colloid Science, 18: 820, (1963).

22. Grim, R.E. Applied Clay Mineralogy , McGraw-Hill,New York (1962).

23. Van Olphen, H. Internal Mutual Flocculation in Clay Suspensions, J. Colloid Science , 19: 313, (1964).

24. Aylmore, L.A.G. and J.P.Quirk. The Structural Status of Clay Systems, Clays and Clay Minerals , Proc. 9th National Conference on Clays and Clay Minerals, pp: 104, (1960).

25. Plesch, P.H. and R.H.S. Robertson. Adsorption on the Ionogenic Surfaces, Nature, 161: 1020, (1948).

26. Faruqi, F.A., S.Okuda and W.O. Williamson. Chemisorption of Methylene Blue by Kaolinite. Clay Minerals, 7:19, (1967).

27. Fairbairn, P.E. and R.H.S. Robertson. Liquid Limit and Dye Adsorption, Clay Min. Bulletin , 3: 129, (1957).

28. Robertson, R.H.S. and R.M. Ward. Assay of Pharmaceutical Clays. J. Pharm. Pharmacol , 3: 27, (1951) .

29. Ramachandran, V.S., K.P. Kacher and N.K. Patwardhan. Adsorption of Dyes by Clay Minerals, Am. Mineralogist , 47: 165, (1962).

30. Nevins, M.J. and D.J. Weintritt . Determination of Cation Exchange Capacity by Methylene Blue Adsorption. Am. Ceramic Soc. Bulletin, 46: 587, (1967).

31. Kipling, J.J. and R.B. Wilson. Adsorption of Methylene Blue in the Determination of Surface Areas, J. Appl. Chemistry, 10:109 ,(1960).

32. Worrall, W. Adsorption of Basic Dyestuffs by Clays. Trans. of Brit. Ceramic Soc , 57: 210, (1958).

33. Markert, S. Determination of the Selectivity Coefficient of Methylene Blue in Comparision with Ca^{++}, K^{+} and H^{+} ions Adsorbed on clay Minerals. Albrecht-Thaer-Arch (Ger) , 9: 521, (1965). (Chem. Abs. 63, 17184, 1965).

34. Miss Allingham, M.M. and J.M. Cullen. Adsorption of Dyes and Related Compounds by Silica, J. Appl. Chemistry, 8: 108,(1958).

35. Fialkov, Ya. A. Adsorption Properties of Kaolinite. J.Appl. Chemistry (USSR) , 18: 221, (1945) (Chem.Abs. 40,3035,1946).

36. Tsuchia, R.T. Decolorizing action of various Clays, J.Chem.Soc.Japan, 70: 88, (1949). (Chem.Abs.45;4419, 1951).

37. Mocik, S. Sorption of Methylene Blue and Methylene Violet on the variously processed Fintice Bentonite , Chem.Zvesti, 18:777,(1964). (Chem.Abs. 53, 54, 1965).

38. Kwun, O.C. Acidity and Adsorption, Mechanism of Solid-Acid. Chem. Abs. 65: 3041, (1966).

39. Merabishvilli, A.A. Effect of Acid Treatment of Clay on Adsorption, J.Phy. Chem.(USSR) , 18: 222, (1945).

40. Hofmann, U and I. Dammler. Methylene Blue Adsorption on to Montmorillonite, Chimia, 23: 476,(1969) . (Chem.Abs.72, 36113,1970).

41 Ramachandran, V.S. et al . Basic Dyestuffs in Clay Mineralogy, Nature , 191: 696, (1961).

42. Leont'eva, A.A. An attempt to apply Thermal Analysis to the Study of Adsorption Processes, J. Phys. Chem. (USSR), 18: 469, (1964). (Chem. Abs. 39, 2918, 1945).

43. Ivanova, A.A. et al . Nature of Clay Mineral Reaction of Organic Dyes and Luminophors, Gliny. Ikh Mineral , 1067: 110, (1970). (Chem. Abs. 74, 101569, 1971).

44. Giesiking, S.S. X-ray Observations of Dye-Clay Complex, Soil Science, 47: 1, (1939).

45. Theng, B.K.G., D.J. Greenland and J.T. Quirk. Adsorption of Alkyl Ammonium Cations by Montmorillonite. Clay Minerals, 7:1 , (1967).

46. Allaway, W.H. and R.E.Grim. Reaction of different Clay Minerals with some Organic Cations. J. Am. Ceramic Soc. 30:137, (1947).

47. McEwan, D.M.C. Clay Mineral Complexes with Organic Liquids. Clay Min. Bulletin , 2: 44, (1948).

48. Bodenheimer, W. and L. Heller. Sorption of α Amino Acids by Copper Montmorillonite, Clay Minerals , 7: 167, (1967).

49. Bulusu, K.R. Decolourisation of Pulp Mill Liquor. 1st Symp. on Ind. Waste Treatment, I.I.T. Kanpur , pp: 525, (1968).

50. Sawyer, C.N. Chemistry for Sanitary Engineers, McGraw-Hill London, pp: 232, (1960).

51. Weber, W.J. Jr. and J.C.Morris. Kinetics of Adsorption on Carbon From Solutions. J. A.S.C.E. San. Engg. Div., 89, SA2 : 31,(1963).

52. Chrisco, H.F. et al. The Effect of Precipitants on Textile Waste Liquors, Sewage Works J., 5: 675, (1933).

53. Black, C.A. Methods of Soil Analysis. Am.Soc. of Agronomy, Inc. Wisconsin, U.S.A. pp: 899, (1965).

APPENDIX 'A'

FREUNDLICH ISOTHERM FOR PHYSICAL ADSORPTION IN EXCESS OF CE C OF CLAYS

METHYLENE BLUE - MONTMORILLONITE SYSTEM

X/M $\frac{m.eq}{g}$	1000 X/M	log 1000 $\frac{X}{M}$	Equlib.concn. C m.eq	1000 C	log 1000 C
0.048	48	1.6812	0.264	264	2.4216
0.08	80	1.9031	0.624	624	2.7952
0.1	100	2.0000	1.39	1390	3.1430
0.12	120	2.0792	2.91	2910	3.4639

METHYLENE BLUE - KAOLINITE SYSTEM

0.01	10	1.0000	0.007	7	0.8451
0.034	34	1.5315	0.0155	15.5	1.1903
0.074	74	1.8692	0.004	4	0.6021
0.102	102	2.0086	0.091	91	1.9590
0.15	150	2.1761	0.128	128	2.1072
0.17	170	2.2304	1.02	1020	3.0086

CONSTANTS OF FREUNDLICH ISOTHERM

ADSORPTION SYSTEM	K	$\frac{1}{n}$
Methylene Blue - Kaolinite	41.6	0.188
Methylene Blue - Montmorillonite	14.15	0.253

APPENDIX 'B'

DATA FOR FREUNDLICH ISOTHERM

METHYLENE BLUE - ACTIVATED CARBON

X mg	M g	X/M mg/g	C mg/l	log X/M	log C
84.15	1	84.15	15.85	1.9	1.21
124.88	1.2	89.13	25.12	1.95	1.405
160.19	1.5	106.5	39.81	2.03	1.6
336.9	2.5	125.9	63.1	2.1	1.8
402	4	100.5	98	2.04	1.9912

SULFUR BLUE - ACTIVATED CARBON

37	1	37	63	1.5682	1.7993
60	2.5	26.92	40	1.43	1.6021
74.88	3	24.63	25.12	1.3914	1.4
84.15	4	20.04	15.85	1.3018	1.2

CONSTANTS OF FREUNDLICH ISOTHERM

ADSORPTION SYSTEM	K	$\frac{1}{n}$
Methylene Blue - Activated Carbon	72.5	0.2
Sulfur Blue - Activated Carbon	17.35	0.33